CHAPTER 1

INTRODUCTION

1.1 HISTORICAL BACKGROUND

Corrosion is as old as the earth itself. Known to people as rust, corrosion is an undesirable phenomenon which destroys the luster and beauty of the materials and lessens their life. Since ancient times corrosion has affected not only the quality of daily lives of the people, but also their technical progress. It is a natural process of destruction like earthquakes, floods, volcanic eruptions etc. with one major difference that we can be only a silent spectator to the above processes of destruction, whereas corrosion can be prevented or at least controlled. Corrosion is the loss of useful properties such as malleability, ductility, electrical conductivity and optical reflectivity by metal due to attack of the environment.

1.2 DEFINITION OF CORROSION

The process whereby a material breaks into its constituent atoms because of the chemical reactions with its surrounding is called Corrosion. Rusting of a metal is a commonly known type of electrochemical corrosion. In rusting, the metal actually undergoes electrochemical oxidation with oxygen as an oxidant. The metal oxide (rust) is then formed. This metal oxide (rust) is the damage that is of serious concern to most industries all over the world.
Corrosion is not only limited to metals, it can also take place on other materials such as polymers and ceramics. Amongst many metals, corrosion is experienced strongly in iron and steel. This is because the oxide that is formed during the process of oxidation does not hold firmly to the surface of the metal, as a result it moves off the metal easily.

Corrosion is a natural process driven by energy considerations. The process of extraction of metals from their ores stores up vast quantity of energy in the metal. Corrosion is therefore a means of releasing this stored–up energy. The metal because of its high energy is in an excited state or state of high energy. The corrosion process is a means of going to the lower energy state (the combined state).

Corrosion is an irreversible interfacial reaction of a material with its environment which results in consumption of the material or its dissolution into the material of a component of the environment. It is the natural tendency of the elements of a material to return to their most thermodynamically stable state (West 1986). It involves an electrochemical process governed by reactions on an atomic level, and basic stress environment variables like pH, temperature, pressure add to the complexity of corrosion.

The term corrosion is also sometimes applied to the degradation of plastics, concrete and wood, but generally refers to metals. Metallic corrosion is the natural process of the metal going to its oxidized state (Shrier 1978). The metal gets corroded by exposure to corrosive atmosphere like moist air, salty water, refinery oil, various acids etc. The most widely used metal is iron (usually as steel).

Several definitions of corrosion have been given; some of them are reproduced below:
Corrosion is the surface wastage that occurs when metals are exposed to reactive environments.

Corrosion is the result of interaction between a metal and environment which results in this gradual destruction.

Corrosion is an aspect of the decay of materials by chemical or biological agents.

Corrosion is extractive metallurgy in reverse. Iron is made from hematite by heating. Iron corrodes and reverts to rust after completing its life cycle. The hematite and rust have the same composition.

Corrosion is the destruction or deterioration of metals as a result of reaction with its environment (Fontana 1987).

Corrosion can also be defined as the gradual destruction of metal, be an unwanted or unintentional chemical or electrochemical attack by its environment beginning at its surface (Dara 1986).

Corrosion may be defined as the loss of useful properties of a material as a result of chemical or electrochemical reaction with its environment (Rajnarayan 1988).

Corrosion is destructive attack of a metal by chemical or electrochemical reaction with the environment (Uhlig 1991).

1.3 THE CONSEQUENCES OF CORROSION

The consequences of corrosion are many and varied, and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass of metal. Failures of
various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. Some of the major harmful effects of corrosion can be summarized as follows:

- **Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown.** When the metal is lost in localized zones so as to give a crack-like structure, very considerable weakening may result from quite a small amount of metal loss.

- **Leaking containers, storage tanks, water and oil transportation lines and fuel tanks cause significant loss of product and may generate severe accidents and hazards.**

- **Loss of time in availability of profit-making industrial equipment.**

- **Reduced value of goods due to deterioration of appearance.**

- **Corrosion products may contaminate chemicals, pharmaceuticals, dyes, packaged goods with direct consequences to consumers.**

- **Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings.**

- **Loss of technically important surface properties of a metallic component.** These could include frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.
• Mechanical damage to valves and pumps or blockage of pipes by solid corrosion products cause loss of efficiency.

• Added complexity and expense of equipment which needs to be designed to withstand a certain amount of corrosion, and to allow corroded components to be conveniently replaced.

• Nuclear hazard like the Chernobyl disaster of 1986 is a living example of transport of radioactive corrosion products in water which are fatal to human, animal and biological life.

1.4 CHEMISTRY OF CORROSION

Metals are opaque, lustrous elements that are good conductors, malleable and ductile. In Chemistry, metals may be defined as elements that readily form cations (positive ions) and form metallic bonds with other metal atoms and ionic bonds with non-metals. Metals may also be described as a lattice of positive ions surrounded by a cloud of localized electrons. The metallurgist considers metals as elements that have overlapping conduction bands and valence bands in their electronic structure.

Metals are obtained from their ore by the expenditure of large amounts of energy. Metals store heat as potential energy during the melting and refining process and release this energy during the corrosion process after reacting with the environment. These metals can therefore be regarded as being in a metastable state and will tend to lose their energy by reverting to compounds more or less similar to their original states, for example the starting material for iron and steel making and the corrosion product rust has the same chemical composition (Fe₂O₃). The energy stored during melting and released during corrosion supplies the driving potential for the corrosion process to take place. Since most metallic compounds, and especially
corrosion products, have little mechanical strength, a severely corroded piece of metal is quite useless for its original purpose (Jain and Jain 2002). Metals such as Mg, Al, Zn, and Fe which require larger amount of energy for refining are more susceptible to corrosion than metals which require lesser amount for refining such as gold, silver, platinum. A corrosion cycle is shown below (Figure 1.1).

![Figure 1.1 Corrosion process](image)

1.4.1 Corrosion Components

No metal would corrode until it has the following four essential components which constitute a corrosion cell.

- Anode
- Cathode
- Electrolyte
- Metallic path
1. Anode: It is the site where oxidation occurs. An anodic reaction is accompanied by loss of electrons. Typical anodic reaction is given below.

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \]

\[ \text{Al} \rightarrow \text{Al}^{3+} + 3e^- \]

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \]

\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \]

2. Cathode: It is the site where reduction takes place. The electrons released at the anode travel to the cathode by a metallic path where they react with the ions in the electrolyte and cause reduction of the positive ions. The cathodic reaction is accompanied by a gain of electrons.

Following are the major cathodic reactions in corrosion of metals in aqueous solution.

\[ 2\text{H}^+ + e^- \rightarrow \text{H}_2 \]

\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \text{ (in acid solution)} \]

\[ \text{H}_2\text{O} + \text{O}_2 + 4e^- \rightarrow 4\text{OH}^- \text{ (in neutral solution)} \]

3. Electrolyte: It provides a conductive medium for passage of ions which acts as charge carriers, like \( \text{Fe}^{2+} \) ions, which carry a positive charge and flow from anode to cathode.

4. Metallic path: It provides the flow of electrons from the anode to cathode. All metals provide the electron path.
All the four components are shown in the Figure 1.2. The flow of electric current is also shown.

**Figure 1.2 Components of corrosion**

1.5 **MECHANISM OF CORROSION**

Iron and steel are important construction materials and it is necessary to understand how they corrode in an aqueous media. Let us consider a piece of iron immersed in aerated water containing one anode and one cathode end as shown in Figure 1.3.

**Figure 1.3 Formation of rust**
All corrosion reactions are electrochemical in nature. At anodic sites on the surface, the iron goes into solution as ferrous ions, thus constituting the anodic reaction. The loss of electron leaves positively charged ions at the anode which travel from the anode to cathode through the water and carry a positive current. The electrons which are released on the anode travel from the anode to cathode through the metallic circuit. These electrons are utilized in the reduction of oxygen present in the water which is in contact with the cathode.

At cathodic site, the electrons react with some reducible component of the electrolyte and are themselves removed from the metal. The corroding piece of metal is described as a “mixed electrode” since simultaneous anodic and cathodic reactions are proceeding on its surface. The mixed electrode is a complete electrochemical cell on one metal surface. Iron can serve as an anode and oxygen gas as the cathode in an electrochemical cell with the salt bridge as an aqueous solution of ions. The most common and important electrochemical reactions in the corrosion of iron are thus,

Anodic reaction

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \]

Cathodic reactions

\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \] (If water is acidic)
\[ \text{O}_2 + \text{H}_2\text{O} + 4e^- \rightarrow 4\text{H}^+ \] (If water is basic)

The negatively charged \( \text{OH}^- \) ions react with the positively charged \( \text{Fe}^{2+} \) ions and form \( \text{Fe}(... \)
4 Fe(OH)$_2$ + O$_2$ + H$_2$O $\rightarrow$ 2Fe$_2$O$_3$ (Brown)

The end product Fe$_2$O$_3$ is called as “rust”. The rust is formed a little away from the surface. The corrosion produced layers are insulators and the iron is protected as long as it is covered by a thin layer of oxides, however, as soon as the oxide layer is damaged, corrosion is accelerated.

The processes involved in the electrochemical cell can be illustrated by the Figure 1.4 below.

**Figure 1.4 Processes involved in the electrochemical cell**

In dry conditions (where there is no moist) such as in places like desert, corrosion is much less slower than in a moist area carrying oxygen (O$_2$). There are many other factors that influence the rate of corrosion of mild steel, including the presence of salt. This is true because the molten salt increases the conductivity of the aqueous solution that is formed at the surface of the metal. Because the conductivity is increased, the rate of electrochemical corrosion increases. The temperature of the system also affects the rate of corrosion of mild steel.
1.6 LOSSES DUE TO CORROSION

Corrosion cannot be defined without a reference to environment. All environments are corrosive to some degree. Some of the typical environments are (i) air and humidity (ii) fresh, distilled, salt and marine water (iii) natural, urban, marine and industrial atmosphere (iv) steam and gases, like chlorine, ammonia, hydrogen sulphide, sulphur dioxide and oxides of nitrogen (v) acids, alkalies soils, (vi) fuel gases. It therefore may be observed that corrosion is a potent force which destroys economy, depletes resources and causes costly and ultimately failures of plants, equipments and components. Corrosion of metals is a chemical or electrochemical reaction between them and their environments, which results in their deterioration and destruction. The enormous loss that takes place continuously due to corrosion may be divided as follows:

1.6.1 Waste of Material and Energy

The loss due to corrosion in India is estimated to be around ₹ 20,000 cores per year. Besides, 10% of the annual output goes for the
replacement of the corroded materials. The successful application of the available knowledge can effect a saving of ₹ 3000 to ₹ 5000 cores annually. Loss due to corrosion has been reported to account for more failures in terms of cost and tonnage than any other environment.

1.6.2 Economical Losses

It is divided into (i) Direct loss and (ii) Indirect loss.

1.6.2.1 Direct loss

Direct loss involves the cost of protection against corrosion and the expenses of the replacement of the corroded components. It includes over design to allow for corrosion, inability to use otherwise desirable materials, the cost of repair of the corroded metal and the cost of anti-corrosive painting or other protection methods.

1.6.2.2 Indirect loss

Indirect loss is much higher and incalculable. Loss due to shut down, loss of efficiency, over design, loss and contamination of products, high maintenance cost, loss of production, extra working capital, damage of equipment, unpredictable machinery failure with consequent costly break down and even explosion, safety and appearance.

1.6.3 Environmental and Health Impact

In recent years, there is increasing use of metals in various fields of technology. Prosthetic devices in the body such as pins, screws, plates, hip joints, pacemaker and other implants involve the use of metals. Though new alloys and better techniques of implantation have been developed, problems such as inflammation caused by corroded products in the tissue around
implants, failures through broken connection in pacemaker still exits. Corrosion leads to loss of life. Fire can occur due to leakage of gas or flammable liquid from corroded pipes.

1.7 IMPORTANCE OF CORROSION STUDIES

Corrosion studies have also become important due to increasing awareness of the need to conserve the world’s metal resources. Virtually all metals suffer corrosion, so its effect permeates in nearly every aspect of human endeavor and this fact alone should make the study of corrosion more important.

It is necessary to pay more attention to metallic corrosion than it was done earlier due to:

- Increasing use of metals in all fields of technology.
- Use of rare and expensive metals whose protection requires special precautions.
- Strict safety standards of operating equipments which may fail in a catastrophic manner due to corrosion.
- Use of new high strength alloys which are usually more susceptible to certain types of corrosive attack.
- Increasing pollution of air and water resulting in a more corrosive environment.

1.8 PRINCIPLES OF CORROSION

Corrosion resistance of a material depends on many factors. Corrosion is adjoined by the following principles (Glasston 1942).
1.8.1 Metallurgical Principles

The corrosion behavior of a metal is well understood by metallurgical principles. In many cases, the metallurgical structure of an alloy can be changed so as to improve its corrosion resistance.

1.8.2 Physical and Chemical Principles

The mechanism of corrosion reactions, the surface conditions of metals and other basic properties are understood by the physical and chemical principles.

1.8.3 Thermodynamic Principles

Thermodynamic principles are applicable to corrosion processes involving free energy, electrical double layer, Nernst equation for electrode potentials and Pourbix diagrams.

Corrosion is the natural tendency of the elements of a material to return to their most thermodynamically stable state. Corrosion occurs in a given environment because of thermodynamic instability of a material in that environment. Thermodynamics indicate the spontaneous direction of a chemical reaction. It is used to determine whether corrosion is theoretically
possible or not. Different metals have different tendencies to corrode in a given corrosive environment. The tendency to corrode depends upon the energy associated with chemical reaction taking place during corrosion. By calculating the amount of free energy change associated in given chemical reaction, it is possible to predict whether natural corrosion can take place in a given set of environmental conditions. Thermodynamics approaches have been also widely used to explain and understand the fundamental corrosion problems.

Thermodynamic stability of chemical compound is determined by the sign and the change in free energy (G) when they are formed from substance. If \( G_1 \) corresponds to the initial free energy of metals and \( G_2 \) to that of reaction products and then \( G_2 - G_1 = \Delta G \) is the free energy change for the reaction. The magnitude of \( \Delta G \) is a measure of the tendency of any chemical reaction, including the reaction of a material with its environment to proceed or not. A large negative value of \( \Delta G \) indicates a pronounced tendency for the reaction to proceed, whereas a positive value indicates no tendency to proceed. If \( \Delta G = 0 \), the system is in equilibrium (Davies 1940).

### 1.8.4 Electrochemical Principles

The corrosion behaviour of the metal is determined by electrochemical principles. The corrosion reaction can be represented by partial reactions such as metal oxidation and reduction of some reducible species of the environment both occurring simultaneously at equal rates of the mixed potential of the reaction. Corrosion reaction mainly occurs at the metal environment interface (Wagner and Traud 1938).

Reaction that can be divided into two or more partial reactions of oxidation and reduction is termed as electrochemical reaction. When a metal is placed in aggressive environment, the metal loses electrons and forms
positively charged ions. The electron flow through the metal and transport of charged particles (cation and anion) across the metal-environment interface generate electric current which brings about the corrosion process. The oxidation of metal to its ion takes place at anode and reduction with evolution of hydrogen or oxygen at cathode (Potter 1961).

- **Anode reaction**

  \[ M \rightarrow M^{n+} + ne^- \]

  \[ Fe \rightarrow Fe^{2+} + 2e^- \]

- **Cathode reaction**

  \[ 2H^+ + 2e^- \rightarrow H_2 \]

  \[ O_2 + 2H_2O + 4e^- \rightarrow 4(OH^-) \]

The above anodic and cathodic reactions known as partial reactions occur simultaneously at the same rate on the metal surface. Corrosion occurs through formation of electrochemical cells in which the anode corrodes and the cathode is protected.

### 1.9 THEORIES OF CORROSION

There are three theories of corrosion. They are:

- Homogeneous theory
- Heterogeneous theory
- Mixed potential theory
1.9.1 Homogeneous Theory

A corroding metal irrespective of the presence or absence of any micro heterogeneity can be regarded as a single electrode on which reactions take place. Metal becomes unstable, due to the charge transfer reaction taking place at the interface. Therefore it is necessary that the potential difference across the interface be more negative than the equilibrium potential for the metal dissolution (anodic reaction) or more positive than the equilibrium potential for the electronation (cathodic reaction).

1.9.2 Heterogeneous Theory

According to this theory, corrosion is caused when the metal is exposed towards the moist atmosphere. Here corrosion is caused by local galvanic elements that arise on the surface of the corroding metal, as a result of the chemical structure heterogeneity.

Though many theories have been put forward, the most acceptable theory is electrochemical or acid theory of corrosion (Walker 1907). The other old theories such as Direct chemical attack theory (Bengoung and Stuart 1922), Colloidal theory (Friend 1921) and Biological theory (Reddic and Lindermann 1932) were either proved to form a part of electrochemical theory or found to be rarely applicable. The factors that are mainly responsible for corrosion are those associated with the metal, environment or both.

1.9.3 Mixed Potential Theory

According to the mixed potential theory, any electrochemical reaction can be divided into two or more partial oxidation and reduction reactions (Perez 2010). There can be no net accumulation of electrical charge
during an electrochemical reaction. That is metal immersed in an electrolyte cannot spontaneously accumulate electrical charge. During the corrosion of an electrically isolated metal sample, the total rate of oxidation must be equal to total reduction (Husler 1985).

The polarization curves for corroding metal can be demonstrated by applying the mixed potential theory. If the attack is uniform the whole surface may be considered as anode for metal oxidation reaction and as cathode for the reaction involving reduction of corrosive agent. When the polarization occurs at the cathode, it is said that the corrosion is under cathodic control. When the polarization occurs at the anode, the corrosion is said to be under anodic control. In majority of cases polarization occurs to some degree at both anodes and cathodes and the corrosion is then said to be under mixed control. The extent of polarization depends not only on the nature of the metal and electrolyte, but also on the actual exposed area of the electrode (Putilova et al 1985).

The three essential parts of a corroding metal are:

- An electron sinks area, where de-electronation reaction occurs.
- An electron source area, where electronation reaction occurs.
- An ionic conductor, to keep the ion current flowing.

1.10 CLASSIFICATION OF CORROSION

Corrosion has been classified in a number of ways. One method classifies it into high temperature and low temperature corrosion. Another method classifies it into wet and dry corrosion. However the most preferred classification is based on the mechanism which separates corrosion into electrochemical and chemical corrosion (Rajnarayan 1988).
1.10.1 Electrochemical or wet Corrosion

Electrochemical corrosion involves aqueous solution or electrolytes and accounts for the greatest amount of corrosion by far.

1.10.2 Chemical or dry Corrosion

It occurs in the absence of a liquid phase or above the dew point of the environment. Dry corrosion is most often associated with atmospheric conditions such as high temperature, air pollutants and moist air.

1.10.2.1 Atmospheric corrosion

Atmospheric corrosion can be classified into four types. Most of them are mixed and have no clear lines of demarcation. Further, the type of atmosphere may vary with the wind pattern, particularly where corrosive pollutants are concerned. The types of atmosphere are marine, industrial, urban and rural environments. (Fontana 1987).

a. Marine environment

The marine environment is characterized by proximity to ocean and salt laden air that can produce very severe corrosion damage on many structural materials and accelerate deterioration of protective coating systems. The salt deposition rate in marine area is 5-1500 mg of sodium chloride/m$^2$ per day (Johnson 1981).

b. Industrial environment

Industrial environment is associated with a host of industries emitting pollutants like oxides of sulphur (sulphur dioxide and sulphur trioxide), oxides of nitrogen (nitrogen dioxide and nitrogen trioxide).
Ammonia and its salts and hydrogen sulphide. The presence of these contaminants in an industrial atmosphere plus dew or fog produces a highly corrosive wet acid film on the exposed surface.

c. **Urban environment**

In this environment the contaminants are usually nitrogen dioxide and carbon dioxide species from automobile exhaust fumes and sulphur dioxide from long range transport.

d. **Rural environment**

The rural atmosphere does not contain strong chemical contaminants but does contain organic and inorganic dust. Its principal corrosive constituents are moisture and some gases such as oxygen and carbon dioxide. Amount of carbon dioxide present in rural atmosphere is 0.03 - 0.05%.

### 1.11 FORMS OF CORROSION

It is convenient to classify corrosion by the forms in which it manifests itself. It is classified into two forms (Fontana 1987).

1. Intrinsic mode of corrosion: general corrosion, pitting corrosion, intergranular corrosion, dealloying and stress corrosion cracking.

2. Extrinsic mode of corrosion: galvanic corrosion, crevice corrosion, fretting corrosion and corrosion due to fatigue.
1.11.1 Intrinsic Modes of Corrosion

(i) General corrosion

This general corrosion also called as a Uniform attack is the most common form of corrosion. It is normally characterized by a chemical or electrochemical reaction which proceeds uniformly over the entire exposed surface or over a large area. The metal becomes thinner and eventually fails.

(ii) Pitting

Pitting is a form of extremely localized attack that results in holes in the metal. These holes may be small or large in diameter, but in most cases they are relatively small. Pits are sometimes isolated or so close together that they look like a rough surface. Pitting is one of the most destructive and insidious forms of corrosion.

(iii) Intergranular corrosion

Localized attack at and adjacent to grain boundaries, with relatively little corrosion of the grains, is intergranular corrosion. The alloy disintegrates (grains fall out) and/or loses its strength. Intergranular corrosion can be caused by impurities at the grain boundaries, enrichment of one of the alloying elements or depletion of one of these elements in the grain-boundary areas.

(iv) Dealloying

Dealloying otherwise known as parting or selective leaching is the removal of one element from a solid alloy by corrosion processes. It is a rare form of corrosion found in copper alloys, cast iron and some other alloys. It occurs when the alloy loses the active component of the metal and retains the
most corrosive resistant component as a porous “sponge” on the metal surface. The best examples are dezincification and graphitization. Aluminum alloys, copper-nickel, copper-silicon and stainless steel alloys are affected by this type of corrosion.

a) **Dezincification**

This occurs in copper-zinc alloys containing more than 15% zinc content. Zinc is more reactive than copper. When exposed to appropriate environmental conditions, zinc readily leaches from brass, leaving pure copper with poor mechanical properties. It is easily recognized by red coloured surface.

b) **Graphitization**

It is the selective leaching of iron from grey cast iron leaving weak, porous and inert graphite. It is a slow process and occurs in relatively mixed corrosion environment. When old graphitized pipes are disturbed, hazardous chemicals escape and contaminate the surrounding soil and sometimes cause fatal explosion and fire.

(v) **Stress-corrosion cracking**

Stress-corrosion cracking refers to cracking caused by the simultaneous presence of tensile stress and a specific corrosive medium. During stress-corrosion cracking, the metal or alloy is virtually unattacked over most of its surface, while fine cracks progress through it.
1.11.2 Extrinsic Modes of Corrosion

(i) Galvanic or bi-metal corrosion

A potential difference exists between two dissimilar metals in electrical contact, when placed in an electrolyte and results in the flow of current between them. Several investigators have shown that corrosion is directly proportional to the area ratio of the cathodic metal to anodic metal. Galvanic corrosion is maximum at the junction of the two metals. The attack decreases with increasing distance from the junction. The metals higher in electrochemical series undergo corrosion.

(ii) Crevice corrosion

Intense localized corrosion frequently occurs within crevices and other shielded areas on metal surfaces exposed to corrosives. This type of attack is usually associated with small volumes of stagnant solution caused by holes, gasket surfaces, lap joints, surface deposits, and crevices under bolt and rivet heads.

(iii) Fretting corrosion

The rapid corrosion that occurs at the interface between contacting highly loaded metal surfaces when subjected to slight vibratory motions is known as fretting corrosion. It is another form of erosion corrosion.

Erosion corrosion is the acceleration or increase in rate of deterioration or attack on a metal because of relative movement between a corrosive fluid and the metal surface. This movement is quite rapid and mechanical wear effects or abrasions are involved. Metal is removed from the surface as dissolved ions or it forms solid corrosion products which are mechanically swept from the metal surface. Erosion corrosion is characterized
in appearance by grooves, gullies, waves, rounded holes, and valleys and usually exhibits a directional pattern. It is also called impingement corrosion.

(iv) **Corrosion fatigue**

Corrosion fatigue is a special case of stress corrosion caused by the combined effects of cyclic stress and corrosion. This results in the drastic reduction in the fatigue life of the metal parts which are dynamically loaded in the moist or corrosive environment.

1.11.3 **Microbiological Corrosion**

Microbiological corrosion is corrosion caused by the metabolic activity of various microbes. It can be controlled by biocides or conventional corrosion control method.

1.11.4 **Filliform Corrosion**

Filliform corrosion is a special case of crevice corrosion which results in irregularly developed hair fine lines or filaments of corrosion. For example, products below coatings of paints, rubber, lacquer, tin, silver, enamel, paper, etc. are affected. It not only weaken the components but affects the surface appearance and may thereby affect the sale potential of such components.

1.11.5 **Exfoliation**

The loss of metals as layers or leaves from a solid metal or alloy is called exfoliation. This type is observed mostly in wrought products. Further Al-Mg, Al-Cu, Al-Zn and Al-Mg-Si alloys undergo exfoliation.
1.11.6 Cavitations Corrosion

This is a special type of corrosion caused due to the formation of vapour bubbles in a corrosive environment near a metal surface and when the bubbles collapse, attack arises. For example hydraulic turbulence, ship propellers.

Generally, these different forms of corrosion can be divided into three categories namely,

GROUP I - Those which can be observed by the naked eye (general, localized and galvanic corrosion).

GROUP II - Those which can be recognized with the assistance of some means of examination (velocity related intergranular, dealloying corrosion).

GROUP III - Those which can only be identified by using microscopes.

1.12 FACTORS INFLUENCING CORROSION

The extent and rate of corrosion depend on nature of metals and environments (Dara 1986).

![Diagram showing the factors influencing corrosion]

- Corrosion
  - Nature of metal
  - Nature of corroding environment
1.12.1 **Nature of the Metal**

- Position in galvanic series
- Overvoltage
- Relative area of anodic and cathodic parts
- Purity of the metal
- Physical stage of the metal
- Nature of the surface film
- Passive character of the metal
- Solubility of corrosion products
- Volatility of the corrosion products.

1.12.2 **Nature of the corroding environment**

- Temperature
- Humidity of air
- Presence of impurities in water
- Presence of suspended particles in atmosphere
- Influence of pH
- Nature of dissolved gases, dissolved salts, pollutants, etc.
- Conductance of the corroding medium
- Formation of oxygen concentration cell
- Flow velocity of process steam
- Polarization of electrodes.
1.13 FACTORS CONTROLLING CORROSION RATE

Certain factors tend to accelerate the action of a corrosion cell. These include:

- Establishment of well-defined locations on the surface for the anodic and cathodic reactions. Metals having a more positive (noble) potential in the galvanic series will tend to extract electrons from a metal which is in a more negative (base) position in the series and hence accelerate its corrosion when in contact with it.

- Stimulation of the anodic or cathodic reaction. Aggressive ions such as chloride tend to prevent the formation of protective oxide films on the metal surface and thus increase corrosion.

1.13.1 Rate of Corrosion

The process of corrosion involves a weight loss of the material or substance. This loss per unit time is used to express the rate of corrosion. The rate of corrosion depends on the material being corroded. There are materials that are not capable of producing a passive film and those that are capable. The rate of corrosion in those substances that have the ability to form a passive film is much slower in comparison to those that do not have the capability to produce the passive film. When a thin protective layer oxide (passive film) is formed on the surface of the metal, the phenomenon is known as passivation.

The rate at which the attack takes place is of prime importance and is usually expressed in one of the two ways:
- Weight loss per unit area per unit time, usually mdd (milligrams per square decimeter per day).

- Decrease in thickness per unit time i.e., rate of penetration or the thickness of metal lost. This may be expressed in American units, mpy (mils per year) or in metric units or mmpy (millimeters per year).

1.14 CORROSION CONTROL METHODS

Corrosion is destructive and silent operating processes. It poses problems to big as well as small industries. Since corrosion is impracticable to eliminate, the effective corrosion science and engineering lies in controlling rather than preventing it (Rajnarayan 1988).

The practical methods available for the protection of metal against corrosion are diverse. They may be broadly based on,

- Selection of material
- Modification of metals
- Modification of design
- Use of inhibitors
- Modification of corrosive environment
- Modification of surface

These methods can be used individually or in combination. Among the various methods of corrosion control, use of inhibitors is the most efficient and cost effective.
1.15 CORROSION INHIBITORS

1.15.1 Definition of Inhibition

One of the extensively studied topics in the field of corrosion is inhibition. Inhibition is a preventive measure against corrosive attack on metallic materials. Chemical compounds may be used which, when added in small concentrations to an aggressive environment, are able to decrease corrosion of the exposed metal.

1.15.2 Definition of Inhibitor

An inhibitor is a substance which when added to acid solutions minimizes the loss of metal, reduces the extent of hydrogen embrittlement, protects the metal against pitting, reduces over pickling and acid fumes resulting from excessive reaction between the acid and basic metals and reduces acid consumption.

Corrosion inhibitors are substances which when added in small quantity to corrosive environment lower the corrosion rate. They reduce corrosion by either acting as a barrier by forming an adsorbed layer or retarding the cathodic and/or anodic process (Sastri 1998).

National association of corrosion engineering defines inhibitor as a substance which retards corrosion when added to an environment even in small concentration (NACE 1965).

Any corrosion retardation process or the reduction in the oxidation rate of the metal by addition of a chemical compound to the system is caused by corrosion inhibitors (Hackermann and Hurd 1962).
Inhibitors are often easy to apply and offer the advantage of in-situ application (Raja and Sethuraman 2008) without causing any significant disruption to the process.

The use of corrosion inhibitors is one of the best methods of combating corrosion. In order that they can be used effectively, three factors must be considered, namely:

1. Identification of the corrosion problems.
2. The economics of the inhibition process.
3. The compatibility of the inhibitor with the process being used.

Generally, three of the four components of a corrosion cell (anode, cathode, electrolyte and electronic conductor) may be affected by corrosion inhibitors in order to reduce corrosion. The inhibitor may cause:

1. Anodic inhibition by increasing the polarization of the anode
2. Cathodic inhibition by increasing the polarization of the cathode
3. Resistance inhibition by increasing the electrical resistance of the circuit while forming a thin or thick deposit on the surface of the metal
4. Diffusion restriction by restricting the diffusion of depolarizers (e.g. Dissolved oxygen) to the surface of the metal. By so doing the inhibitors play a dual role.

However there are several factors to be considered when choosing an inhibitor.
• Cost of the inhibitor.

• Toxicity of the inhibitor can cause ill effects on human beings and other living species.

• Availability of the inhibitor determines the selection of it.

• Inhibitor should be environment friendly.

1.16 ROLE OF INHIBITORS

Organic and inorganic compounds constitute a large class of corrosion inhibitors, which as a general rule; affect the entire surface of a corroding metal when present in sufficient concentration. Most of the organic/inorganic compounds containing elements of groups V B, VI B or functional groups of the type NH₂, C=O and CHO are known to be effective inhibitors. The principal mechanism suggested by several researchers in the field of corrosion inhibition studies is “adsorption”. The inhibitor is adsorbed on the entire surface of the corroding metal and by doing so prevents attack from the corrodent. Organic inhibitors are adsorbed according to the ionic charge of the inhibitor on the metal’s surface. Cationic inhibitors e.g. amines (positively charged) or anionic inhibitors eg. sulphonates (negatively charged) will be adsorbed preferentially, depending on whether the metal is charged positively or negatively. The inhibitors may therefore be considered as two fundamental types namely,

Type A: Those which form a protective barrier film on anodes or cathodes by reaction between the metal and the environment. The Type A inhibitors function in neutral or in some cases, alkaline solution in which the main cathodic reaction is an oxygen reduction reaction in which the corroding
metal surface is covered by a film oxide or hydroxide. Type A inhibitors tend to produce a protective film or stabilize an already existing ore.

Type B: Those which are initially adsorbed directly onto the metal surface by interaction between surface charges and ionic and/or molecular dipole charges. This division of inhibitor types results principally from the pH of the solution where they operate.

Inhibitors must be present in a minimum concentration for them to be fully effective. When the inhibitor falls below a specified minimum amount, the cover it provides is inadequate and the exposed area becomes a centre for more active corrosion. This is very common with anodic inhibitors. It has been observed that at certain concentrations, inhibitors lose their efficiency and become corrosion promoters. The efficiency of organic inhibitors can be improved in the presence of certain halogen ions. Halogen ions alone are also known to inhibit corrosion to some extent in acid solutions. The efficiency of the corrosion inhibition is in the order; $\Gamma > \text{Br}^- > \text{Cl}^-$. Fluoride does not show inhibition characteristics. Synergism of halogen ions can be attributed to the fact that the metal adsorbs halogen ions whose charge shifts the surface in a negative direction, thereby increasing adsorption of the cationic organic inhibitor. Being able to discover possible compounds that can be used as corrosion inhibitors requires a lot of hard work, innovation and laboratory analysis/synthesis.

1.17 CLASSIFICATION OF CORROSION INHIBITORS

Corrosion inhibitors are briefly classified as follows,
1.17.1 Based on electrode process

(i) Anodic inhibitors

An anodic inhibitor increases the anodic polarization and hence moves the corrosion potential to the cathodic direction and hence also called as passivating inhibitors. A number of inorganic inhibitors such as orthophosphates, silicates etc. fall under anodic type. Even though anodic inhibitors are widely used, a few of them have some undesirable property. If such inhibitors are used in very low concentrations, they cause stimulation of corrosion such as pitting and for this reason anodic inhibitors are denoted as dangerous.

(ii) Cathodic inhibitors

Cathodic inhibitors shift the corrosion potential to the anodic direction. Here the cations migrate towards the cathode surfaces where they are precipitated chemically or electrochemically and thus block these surfaces. The inhibiting action of cathodic inhibitors takes place by three mechanisms,

a. Cathodic poisons: The cathodic reduction process is suppressed by impeding the hydrogen recombination and
discharge but increase the tendency of the metal to be susceptible to hydrogen induced cracking.

b. Cathodic precipitates: Compounds such as calcium, magnesium will precipitate as oxides to form a protective layer which acts as a barrier on the metal surface.

c. Oxygen scavenger: These compounds react with oxygen present in the system to form a product and reduce corrosion.

Eg: As$^{3+}$ and Sb$^{3+}$ on dissolution of Fe in acids.

(iii) Mixed inhibitors

These inhibitors retard both the anodic and cathodic processes. The shift in the potential is smaller and the direction is determined by the relative size of the anodic and cathodic sites. Such inhibitors will have the advantage over other inhibitors in that they control both the cathodic and anodic corrosion reactions and hence are very safe to apply.

1.17.2 Based on environment

(i) Acid inhibitors
a) Inorganic inhibitors

The compounds such as As$_2$O$_3$, Sb$_2$O$_3$ have been reported as inhibitors in acid media. The action of these compounds have been attributed to the deposition of the metal on iron and steel by reduction and raising the hydrogen overvoltage and thereby reducing the corrosion. In strong acid solutions, bromide and iodide have been found to be effective inhibitors. Recently, it is shown that the addition of heavy metal ions such as Pb$^{2+}$, Tl$^+$, Mn$^{2+}$ and Cd$^{2+}$ is found to inhibit corrosion of iron in acids.

b) Organic inhibitors

Usually the corrosion of metals and alloys in acid solution is very severe and this kind of attack can be inhibited by a large number of organic substances. In general, nitrogen, oxygen and sulphur containing compounds with a hydrocarbon part attached to the polar group are used as inhibitors. Triple bonded hydrocarbons, acetylenic alcohols, thiourea, aromatic or heterocyclic compounds containing nitrogen and many other families of simple organic compounds and condensation products formed by the reaction between two different species such as aldehydes and amines are mostly used.

(ii) Alkaline inhibitors

The metals which form amphoteric oxides are prone to corrosion in basic solution. Many naturally occurring organic compounds are often used as inhibitors for metals in basic solutions. Tannins, gelatins, saponins, agar-agar etc. and compounds such as thiourea, substituted phenols, naphthols, β-diketones etc. have been used as effective inhibitors in basic solutions due to the formation of metal complexes.
(iii) **Neutral inhibitors**

Inhibitors which are effective in acidic solutions do not function effectively in neutral solutions, since the mechanism is different in the two solutions. In neutral solutions, the interaction of inhibitors with oxide covered metal surfaces and prevention of oxygen reduction reactions at cathodic sites take place. Such inhibitors protect the surface layer from aggressiveness. Some surface active chelating inhibitors have been found to be efficient inhibitors in near-neutral solutions.

1.17.3 **Based on Mode of Protection**

(i) **Chemical passivators**

Substances which usually have a sufficiently high equilibrium potential (redox or electrode potential) and sufficiently low over potential decrease corrosion rate on attainment of passivity and are called chemical passivators.

Examples:

- Nitrites are used as inhibitors for antifreeze cooling waters.
- Chromates are mostly used as inhibitors for recirculating cooling waters.
- Zinc molybdate is used as an inhibiting pigment for paints.

(ii) **Adsorption inhibitors**

These represent the most widely used class of inhibitors. In general, they are organic compounds which get adsorbed on the metal surface and provide a blanketing effect over the entire surface, i.e. both in cathodic and
anodic cases. Generally they effect both cathodic and anodic reactions equally, but in many cases the effect may not be equal. These are commonly used in the acid pickling of hot rolled products in order to remove the black mill scale and are thus known as pickling inhibitors.

Examples:

- Compounds containing lone pairs of electrons such as nitrogen atoms in amines, quinolines, sulphur atoms in thio compounds and oxygen atoms in aldehydes.

(iii) **Film forming inhibitors**

In contrast to the adsorption inhibitors which form the straight forward adsorbed film of the inhibiting species, many substances called film forming inhibitors, appear to stop corrosion by forming a blocking or a barrier film of a material other than the actual inhibiting species itself. Such materials tend to be specific either to the cathode or to the anode. Zinc and calcium salts are the most common examples of cathodic film forming inhibitors. Benzoate is the common example of anodic film forming inhibitors, which inhibit corrosion during voyages.

(iv) **Vapour phase inhibitors**

Atmospheric corrosion of metals in closed spaces as in parcels during storage and shipment can be prevented by the use of certain substances called vapour phase inhibitors also called as volatile inhibitors. These are substances of low but significant vapour pressure. The vapour comes in contact with the surface of the metal and the adsorption of the inhibitor takes place. The moisture then hydrolyses it and releases protective ions which have corrosion inhibiting properties.
Examples:

- Dicyclohexylamine chromate and benzotriazole for protecting copper.
- Phenyl thiourea and cyclohexylamine chromate for brass.
- Dicyclohexylamine nitrite for ferrous and non ferrous parts.

1.18 THEORIES OF INHIBITION

The inhibitive action of inhibitor has been explained by adsorption theory or film formation theory (Hackermann 1948).

1.18.1 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 and chemical adsorption (Tushar 2004). Organic inhibitors which presumable are not capable of oxidizing or precipitating the metal ion must have the ability to adsorb and impede either anodic or cathodic reaction or both at the metal-electrolyte interface. The different types of adsorption associated with organic inhibitors are,
Electrostatic adsorption or electrosorption

Physical or van der Waals type adsorption

Chemisorption or pi electron adsorption

a) **Electrostatic adsorption**

Electrostatic adsorptions due to the coulombic or electrical forces which stretch out from the metal are much longer in range than the chemical forces which attract the inhibitor molecules on metal surface.

b) **Physical theory**

Physical adsorption is the result of electrostatic attractive forces 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 outer Helmholtz plane of the electrical double layer existing at the metal solution interface. The surface charge can be defined by the open circuit potential ($E_{corr}$) versus potential of zero charge (PZC) of the particular metal. When the difference is negative, cation adsorption is favoured. Adsorption of anions is favoured when it is positive.

c) **Chemisorption**

This process involves charge sharing or charge transfer from the inhibitor molecule to the metal surface in order to form a coordinate type of bond. The chemisorption process takes place more slowly than electrostatic adsorption and with higher activation energy. It is specific for certain metals and it is not completely reversible. Considering the inhibitors as electron donors, electron transfer can be expected with compounds having more loosely bound electrons or with compounds having multiple bonds or
aromatic rings whose electrons have $\pi$ character. When the coverage of metal surface by adsorbed inhibitor increases, lateral interactions between inhibitor molecules may arise leading to stronger adsorption and inhibitor efficiency.

1.18.2 **Film Theory**

This theory revealed that effective protection of metals by inhibitors is due to the formation on the metal surface a layer of insoluble or slightly soluble corrosion products (Putilova et al, 1960 and Husler, 1985).

1.18.3 **Hydrogen Overvoltage**

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

1.18.4 **Quantum Chemical Approach**

Direct interaction between surface metal atoms and the outermost electrons of the organic molecule sometimes lead to chemisorption phenomenon and thereby cause inhibition. Chemisorption of organic inhibitors may be taken as linear combination of the participating wave function of inhibitor molecule as well as of surface metal atoms. The binding energy of the metal inhibitor adduct, may thus be correlated to the energy difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the metal atoms and the inhibitor molecule respectively.
1.19 INHIBITORS FOR MILD STEEL

- A number of nitrogen, oxygen containing compounds have been examined as corrosion inhibitors for mild steel.

- Several salts of arsines, phosphines and triple bonded hydrocarbons, acetylenic alcohols, thiourea, aromatic, heterocyclic compounds are used as corrosion inhibitors for mild steel.

- There are many naturally occurring substances which are used as inhibitors for mild steel. These are heterogeneous or compounds having higher basicity and electron density on the hetero atom.

1.20 TOXICITY OF INHIBITORS

Toxicity is the ability of a chemical to damage an organ system, disrupt biochemical process, and disturb an enzyme system at the site in the body. Very toxic chemicals like chromate induce critical damage to the reproductive system. Systemic poisons include (i) Hepatotoxic agent that damage liver (ii) Nephrotoxic agents that damage kidney (iii) Neurotoxic agents that affect the nervous system and possibly cause neurological damage (iv) Haematopoietic agents that affect the blood and the blood forming tissues and (v) agents that damage the lungs or respiratory system.

Most of the inorganic inhibitors used are toxic substances. The safety and environmental issues of corrosion inhibitors has become a global concern. Chromates which are used in the pretreatment of aluminum alloys are both toxic and carcinogenic. Nitrites get absorbed into the blood stream
and cause death. Some of the nitrite-induced poisoning includes diarrhea, salivation and abdominal pain.

1.21 NATURAL PRODUCTS AS CORROSION INHIBITORS

Environmental friendly corrosion inhibitors range from rare earth elements to organic compounds and are used as alternative corrosion inhibitors to reduce the harmful effects on humans, animals and environment. Plant extracts offer several advantages over traditional inhibitors such as chromates, nitrites, benzoates, phosphates, amines, ammonia etc. Natural products of plants exhibit high surface activity, so the trend of using them has become increasingly important in recent years. Plant extracts are environmental friendly, bio-degradable, non-toxic, easily available and of potentially low cost. About 100 plant materials have been studied as corrosion inhibitors for mild steel, aluminium, zinc, copper and magnesium. Materials from all different parts of the plant viz., leaves, bark, nuts, flowers, fruits, fruit peels, essential oil, pulpy vegetable matter and seeds have been studied as corrosion inhibitors. The nitrogen heterocycles, tannins, oxygen containing hetrocycles like flavones, coumarins and flavonoids are reported to inhibit corrosion. Use of plant extracts offers higher efficiency because corrosion inhibition is fortified through synergism (Wan Nik et al 2011).

1.22 CORROSION MONITORING TECHNIQUES

1.22.1 Methods to Monitor Corrosion

Corrosion techniques are mainly aimed with the objectives of diagnosing and controlling corrosion reaction. The corrosion testing and inhibitor effectiveness can be done by,
Non–electrochemical methods

Weight loss method - Direct measurement
Gasometric method - Direct measurement

Electrochemical methods

Potentiodynamic polarization method - DC polarization/Tafel extrapolation
Linear polarization method - DC polarization resistance
Impedance method - AC electrochemical technique
Faradic distortion method - AC electrochemical technique

1.22.2 Non-Electrochemical Methods

There are number of non-electrochemical methods used to study the efficiency of inhibitors on metal corrosion. Among these weight loss methods and gasometric methods are frequently used.

1.22.2.1 Weight loss methods

This is the most reliable method. This method is still widely used since many different materials can be exposed at one site and unambiguous data on the form of corrosion on the specimen can be obtained. The difference in weight of metal due to corrosion is measured by exposing the metal specimen of known area of the corrosive environment for a known period of
time. The corrosion rate is expressed in millimeter per year and is calculated by,

\[
\text{Corrosion rate} = \frac{87.6 \times W}{D \times A \times T} \text{(mm/y)}
\]

where,

- \( mm/y \) = millimetre per year
- \( W \) = weight loss of the metal in milligrams
- \( D \) = metal density in g / cm\(^3\) (7.86 g / cm\(^3\))
- \( A \) = area of the sample in cm\(^2\)
- \( T \) = time of exposure of the metal surface in hours
- \( 87.6 \) = conversion factor

The effectiveness of an inhibitor is assessed in terms of its inhibition efficiency.

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

1.22.2.2 Gasometric methods

Gasometric method gives accurate results compared to that of conventional weight loss method provided:

- The inhibitor does not react with hydrogen.
- The hydrogen penetration into the metal is small compared to the total volume of the gas.
In this method, the volume of hydrogen gas (in acid corrosion) evolved in the presence and absence of inhibitor are measured directly at a constant temperature and atmospheric pressure using gas volumetric procedures. From the volume of hydrogen gas evolved the corrosion rate can be calculated. The main disadvantage of this method is that they are time consuming.

1.22.3 Electrochemical Methods

Current voltage relationships are commonly used for the measurement of corrosion and are consequently of value in evaluating inhibitors. Most corrosion measurements involve a scan of the working electrode potential and a measurement of the resulting current. This is called as ‘potentiodynamic scan’. If potential is kept constant, the plot of the resulting current as a function of the time is termed as ‘potentiostatic’. It is also possible to control the current at the working electrode and measure the resulting potential which is then called ‘galvanodynamic scan’. Similarly, if a constant current value is maintained and a potential against time curve is generated, the experiment is termed as ‘galvanostatic’.

Electrochemical methods are widely used in inhibitor testing. Since electrochemical corrosion is the result of current flow between anodic and cathodic areas on a metal surface, the effect of the inhibitor is to reduce this current. These techniques require short duration which is a definite advantage and give more accurate results. These include direct current (D.C) and alternating current (A.C) techniques for determining of corrosion rates in systems following simple kinetics.

1.22.3.1 D.C Methods

There are a number of D.C methods available. One such method is discussed below.
Potentiodynamic polarization measurement

Experimentally, one can measure polarization characteristics by plotting the current response as a function of the applied potential. Since the measured current can vary over several orders of magnitude, usually the log current function is plotted against potential on a semi-log chart. In order to measure and control the potential and current flow of a corroding metal specimen, it is necessary to use a three electrode system: the specimen or working electrode, auxiliary electrode and a reference electrode. A typical standard polarization test cell recommended by ASTM G5 could be used for taking the electrode and mounting the electrodes. After connecting the electrodes with proper instrumentation, the potential of the corroding specimen can be changed stepwise at regular intervals or changed continuously at a constant scan rate at a fixed temperature. The current that results for each change in potential is recorded. Thus, a plot of potential against the logarithm of the applied current density provides the polarization curve.

\[
\text{Corrosion rate} = \frac{0.13 \times i_{\text{corr}} \times E.W}{d}
\]

where,

\[
\begin{align*}
  i_{\text{corr}} &= \text{Corrosion current density in } \mu\text{A/cm}^2 \\
  E.W &= \text{Equivalent weight of corroding species in g} \\
  D &= \text{Density of the metal in g/cm}^3 \\
  \text{I.E (\%)} &= \frac{(i_0 - i)}{i_0} \times 100
\end{align*}
\]
where,

\[ i_0 = \text{Corrosion current density of the metal specimen in uninhibited acid.} \]

\[ i = \text{Corrosion current density of the metal specimen in inhibited acid.} \]

The measurement of Open Circuit Potential (OCP) is used for monitoring corrosion, though the corrosion potential itself is difficult to interpret. In this method the metal is covered with 1 ml of the electrolyte solution and OCP measured for an hour. The corrosion potential is used to predict the behavior of metals.

### 1.22.3.2 A.C method - Impedance techniques

Impedance technique has been widely used for the measurement of corrosion rate, due to the main advantage that the double layer capacitance \( (C_{dl}) \) and charge transfer resistance \( (R_{ct}) \) can be determined. The term resistance and impedance both imply a restriction to the current flow. When dealing with D.C, only resistors produces this effect. But in the case of A.C, both inductors and capacitors influence electron flow. The cell impedance is resolved into two parts i.e.

- **Real part** \( Z' = |Z| \cos \theta \) and

- **Imaginary part** \( Z'' = |Z| \sin \theta \).

The charge transfer resistance \( (R_{ct}) \) is related to \( i_{corr} \) as

\[
R_{ct} = \frac{b_a \times b_c}{2.3(b_a + b_c) i_{corr}}
\]
where,

$b_a$ and $b_c$ are Tafel slopes,

$R_{ct}$ is obtained from the impedance plots.

The impedance $Z$ is the total resistance to the alternating current and given by,

$$Z = Z' - Z''$$

where,

$$Z' = R_s + \frac{R_{ct}}{1 + \omega^2 C_{dl}^2 R_{ct}^2}$$

$$Z'' = \frac{\omega C_{dl} R_{ct}^2}{1 + \omega^2 C_{dl}^2 R_{ct}^2}$$

From equation, the plot $Z'$ against $Z''$ for various frequencies results in a semicircle which cuts the real axis at higher and lower frequencies. At higher frequency end, the intercept corresponds to $R_s$ and at lower frequency end; the intercept corresponds to $R_s + R_{ct}$. The difference between these two values gives $R_{ct}$ and from the values, the corrosion rate can be calculated. The double layer capacitance is obtained from the frequency at which $Z''$ is maximum.

$$\omega (Z''_{max}) = \frac{1}{C_{dl} \times R_{ct}}$$
The impedance measurements were carried out for mild steel in acidic media. For measurements of impedance, the cell used was same as that used for potentiodynamic polarization measurements. An A.C potential of 10 mV was super imposed on the steady open circuit potential. A plot of real part ($Z'$) and imaginary part ($Z''$) were made and $R_{ct}$ and $C_{dl}$ were calculated. Impedance measurements were carried out for mild steel in 1N HCl, H$_2$SO$_4$ and H$_3$PO$_4$ without and with inhibitors for the best concentration inhibition efficiency was calculated using the formula,

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

where,

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

$R_{ct} (\text{blank})$ = Charge transfer resistance without inhibitor.

1.22.3.3 Advantages

A.C Methods offer many advantages:

- Data on several cell parameters are obtained quickly and simultaneously.
- High electrolyte resistance is not a problem.
- Applicable to low conductivity systems also.
- Provides mechanistic information.
- No reaction products build up because there is no net current flow (if the D.C component is made zero). This results in the least possible disturbance of cell.
The method is very sensitive. Even small changes in the specimen can alter the impedance plot.

Thus with A.C impedance measurements, it is possible to get more information about various electrochemical process.

1.22.4 Spectroscopic Methods

Fourier transform Infrared (FTIR) and Ultra-Violet (UV-Vis) spectroscopic techniques are useful for knowing the arrangement of inhibitor molecule on the metal surface. The amount of inhibitor adsorbed on the electrode has also been determined by these methods (Zucchini et al 1971). FTIR studies help to predict the functions of adsorption bands and the arrangement of the inhibitor molecule on the surface of the metal. UV-Vis spectroscopy had been used to determine the amount of inhibitor adsorbed on the electrode. Reflection spectra, mass spectra and massbouir spectroscopy are other methods employed for studying corrosion inhibition. Adsorption characteristics can also be deduced from NMR spectra, which give the electron density of the adsorbing molecule (Cox et al 1964).

1.22.5 Other Methods

Methods such as electron microscopy, ellipsometry, magnetic susceptibility, hydrogen permeation, and X-ray and electron diffraction have also been used for studying inhibition phenomenon. X-ray photo electron spectroscopy and Auger electron spectroscopy have also been used to study the mechanism of action of inhibitors (Lewis 1982).

1.22.6 Adsorption Isotherms

Adsorption is a phenomenon where organic compounds get adsorbed on the metal surface and provide a blanketing effect over the entire surface.
An adsorption isotherm is the mathematical expression which relates the bulk concentration of an adsorbing species to its surface concentration at constant temperature.

It gives the relationship between the coverage of an interface with the adsorbed species (i.e. amount adsorbed) and the concentration of species in solution. Plots of the variation in corrosion rate with change in inhibitor concentration have the appearance of being mirror images of adsorption isotherm for most organic inhibitors. This strongly suggests that adsorption of the inhibitor on the metal surface (partly) accounts for the inhibition mechanism.

Various adsorption isotherms have been formulated (Wranglen 1972, Tushar 2004). A list of various isotherms and the corresponding plots is given in the Table 1.1. A common procedure is to convert isotherm to a linear form and plot the experimental data accordingly. This data can be fitted to any one of the adsorption isotherms. From the suitable plot, the free energy of adsorption of the organic inhibitor can be obtained (Hackermann 1948).

Table 1.1 Types of adsorption isotherms

<table>
<thead>
<tr>
<th>Name of Adsorption</th>
<th>Plots</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir Isotherm</td>
<td>C / \theta vs C</td>
</tr>
<tr>
<td>Freundlich Isotherm</td>
<td>Log(\theta / C) vs \theta</td>
</tr>
<tr>
<td>Temkin Isotherm</td>
<td>\theta vs Log C</td>
</tr>
<tr>
<td>Frumkin Isotherm</td>
<td>I.E vs Log C</td>
</tr>
<tr>
<td>Flory Huggins Isotherm</td>
<td>Log(\theta / C) vs Log(1-\theta)</td>
</tr>
</tbody>
</table>
Where $\theta$ is the surface coverage, $C$ is bulk concentration of the solution.

1.23 INDUSTRIAL APPLICATION OF CORROSION INHIBITORS

Metal corrosion happens when metals are exposed to moisture in air. This is because most metals react with oxygen which creates rust and eventually leads to corrosion. The end result of corrosion on various appliances, vehicles, and other items include metal components. A common problem found in industry is corrosion. Without the proper protection, the instruments and machines can be subjected to corrosion, erosion and premature failure leading to expensive repairs and reduced lifetime. In virtually all situations, metal corrosion can be managed, slowed or even stopped by using the proper techniques.

Corrosion of metals can be prevented if the contact between metal and air is cut off. This is done in a number of ways. Some of the methods are:

1. Corrosion can be prevented if the metal is coated with something which does not allow moisture and oxygen to react with it.

2. Coating of metals with paint, oil, grease or varnish prevents the corrosion of metals.

3. Coating of corrosive metals with non-corrosive metals also prevents corrosion.

Plating, painting, and the application of enamel are the most common anti-corrosion treatments. They work by providing a barrier of corrosion-resistant material between the damaging environment and the
structural material. Plating usually fail only in small sections, and if the plating is more noble than the substrate (for example, chromium on steel). A galvanic couple will cause any exposed area to corrode much more rapidly than an unplated surface would. For this reason, it is often wise to plate with active metal such as zinc or cadmium. Painting either by roller or brush is more desirable for tight spaces; spray would be better for larger coating areas. Painting a material that rusts, usually an iron rich material like steel, keeps the metal from exposure to the environment such as air and humidity. Rust is actually the oxidation of metal, and protecting metal with paint does not allow this to happen (Tretheway and Chamberlain 1996). Painting does the following,

a. **Barrier against oxygen**

   Oxidation occurs when the elements in metal and oxygen react and over time cause corrosion. Paint is non-permeable and does not allow oxygen to react with the metal.

b. **Barrier against water**

   Since paint is non-permeable, it also protects surfaces from water. Water causes wood to decay and metal to rust. By painting an item, the water cannot react with metal or soak into wood.

c. **Barrier against debris**

   Wind carries small particles of dust that can deteriorate surfaces over time. By painting a surface, a thin, protective layer is added that may deteriorate, but the integrity of the surface below is not compromised with regular painting.
First, the surface to be painted must be thoroughly prepared. It must be chemically and microscopically clean. To achieve this state, mechanical means such as grinding and buffing are used. Acid baths are also used to remove any surface contaminants. Dirt, grease, oil or chemicals may interfere with adhesion and prevents deposition of paint, which may also interfere with the bonding (Fontana 2010). Painting over loose rust will result in poor adhesion and an uneven finish. A mixture of hydrochloric acid and sulphuric acid is used to dip the metals for cleaning metal surfaces before painting. This process is called “pickling”.

The protective coating method is a passive corrosion protection method. The protective coating isolates the metallic surfaces from the aggressive media, such as moisture, salts, acids etc. Good quality protection is achieved by adding inhibitors.

Corrosion inhibitors are chemicals that react with the metal surface or the environmental gases causing corrosion, thereby, interrupting the chemical reaction that causes corrosion. Inhibitors can work by adsorbing themselves on the metal surface and forming a protective film. These chemicals can be applied as a solution or as a protective coating via dispersion techniques.

1.24 REVIEW OF LITERATURE

1.24.1 Studies Related to Corrosion Inhibition of Mild Steel by Chemicals

Corrosion inhibition of mild steel in 0.67M H₃PO₄ by phenacyl dimethylsulphonium bromide and six of its p-substituted derivatives were studied by Arab and Al-Turkustani (2006) using different chemical, electrochemical and scanning electron microscopy techniques. The order of
increasing efficiency was correlated with its p-substituted derivatives through Hammett relation. Potentiodynamic polarization curves indicated that the compounds acted primarily as mixed type inhibitors.

Eddy et al (2008 b) studied the adsorption and inhibitive efficiencies of 5- amino-1-cyclopropyl-7-[(3R,5S)3,5-dimethylpiperazin-1-YL]-6,8-difluoro-4-oxo-quinoline-3-carboxylic acid (ACPDQC) on mild steel in H₂SO₄ using gasometric and thermometric techniques. ACPDQC inhibited the corrosion through physical adsorption and was spontaneous, exothermic and was consistent with models of Langmuir and Frumkin isotherms.

A new safe corrosion inhibitor guanidine derivative was synthesized and its inhibitive performance towards the corrosion of mild steel in 1M hydrochloric acid and 0.5M sulphuric acid was investigated by Khaled (2008). Studies showed inhibition efficiency up to 99% and 96% in 1M HCl and 0.5M H₂SO₄ respectively. Polarization measurements reveal that the investigated inhibitor was cathodic in 1M HCl and mixed type in 0.5M H₂SO₄.

N’-benzylidene-3-(quinolin-4-ylthio) propanohydrazide was synthesized, characterized and tested as a corrosion inhibitor for mild steel in HCl and H₂SO₄ solution using weight loss method, electrochemical impedance spectroscopy and potentiodynamic polarization methods by Saliyan and Adhikari (2008). The inhibition efficiency increased with increasing temperature. It was found to act as an anodic inhibitor. Chemisorption mechanism was proposed.

Mohammed et al (2008) studied the effect of temperature on the efficiency of succinic acid as an inhibitor for the corrosion of low carbon steel electrode in aerated non-stirred 1N HCl solution. Results obtained showed that the inhibition efficiency decreased with increase in temperature.
indicating the physisorption. The standard free energies of adsorption were lower than 40 kJ mol\(^{-1}\) which also confirmed the physisorption.

Inhibitive and adsorption properties of sparflloxacin for the corrosion of mild steel in HCl was studied using gravimetric, gasometric and thermometric methods of monitoring corrosion. Eddy et al (2008 c) found that the adsorption of sparflloxacin on the surface of mild steel was spontaneous, exothermic and its adsorption characteristics were best described by Langmuir adsorption isotherm.

Change of open circuit potential with immersion time, Tafel polarization and electrochemical impedance spectroscopy were performed by Musa et al (2009 a) to investigate the corrosion inhibitor layer, forming on mild steel surface. 4-Amino-5-phenyl-4H-1,2,4-trizole-3-thiol was used throughout the experiment as the corrosion inhibitor under hydrodynamic conditions with different pickling solutions of 0.5M HCl and 2.5M H\(_2\)SO\(_4\). The hydrodynamic condition of the experiment were simulated using the rotating cylinder electrode. The fitted data recorded from EIS were in line with those of polarization measurements. Tafel polarization, and EIS measurements showed that the formation and development of inhibitor layer in both pickling solutions were, flow velocity dependence.

The inhibition of corrosion of mild steel in hydrochloric acid solutions by 2-benzoylpyridine (2BP) and pyridoxolhydrochloride (2PXO) at 303 K, 313 K and 323 K was investigated by James et al (2009). 2BP exhibited higher maximum inhibition efficiency (78.99\%) than 2PXO (71.93\%). Inhibition was found to increase with increasing inhibitor concentration and decreasing temperature. A first order type of mechanism was deduced from the kinetic treatment and the process of inhibition were attributed to physisorption.
The effect of phenylthiourea as corrosion inhibitor for low carbon steel at different hydrochloric acid concentrations, different temperatures and fixed speed of electrode rotation were addressed in their work by Khadom et al (2009). Maximum inhibitor efficiency of 96% was obtained in 1M HCl at 333 K and 1 g/L inhibitor concentration.

Venkatesan et al (2009) prepared formazan of benzaldehyde and formazan of p-dimethyl aminobenzaldehyde and observed as corrosion inhibitor for mild steel in 1.11N HCl by weight loss method. Kinetic treatment of the results gave first order kinetics. Corrosion inhibition efficiency was explained on the basis of structure dependent-electron donor properties of the inhibitors.

The effect of different temperatures and acid concentrations on the corrosion of mild steel in phosphoric acid were reported by Yaro et al (2010) in their work. A detail of thermodynamic parameters of activation (E, H and S) and kinetic studies for corrosion reaction were obtained. The values of activation energy E and enthalpy of activation H decrease with increase of acid concentration indicating the increase in reaction. Entropy of activation S tends to lower values with increasing of acid concentration which indicated that the activated complex was more orderly relative to the initial state.

The inhibitive effect of substituted 1,3,5-Thiadiazol-2-amines on the corrosion of mild steel in 1M H₂SO₄ was studied. These compounds act as a mixed type with more cathodic character and obeyed Temkin adsorption isotherm. Pi-electrons of aromatic ring and lone pair of electrons of N, O and S atoms present in the five membered rings and in the side chain apparently are able to get adsorbed on the metal surface (Shamita Begum et al 2010).
An attempt was made to explore the possibility of using dicycloimine hydrochloride (DCI) as an inhibitor on mild steel in 1M HCl. The results revealed that DCI acts as an effective inhibitor with 90% of inhibition efficiency in HCl media (Rajalakshmi et al 2010 a).

The corrosion inhibition of mild steel in 1M HCl by pharmaceutically active compound, Primaquine was investigated by weight loss, electrochemical impedance spectroscopy and polarization techniques. Experimental results showed that it was an effective inhibitor for mild steel corrosion in 1M HCl solutions and it exhibited > 90% inhibition efficiency. Potentiodynamic polarization studies showed that primaquine was a mixed-type inhibitor (Ahamad et al 2011).

Anwar Sathiq et al (2011) studied the influence of N-(1-Morpholinobenzyl) urea (MBU) on corrosion inhibition of mild steel in 1M HCl. The experimental results showed that the inhibition efficiency increased with increasing concentration but decreased with increasing temperature. The adsorption of MBU obeyed Temkin’s adsorption isotherm. Potentiodynamic polarization curves showed that the indicator acted as a cathodic inhibitor.

Nalini et al (2011) synthesized a heterocyclic imidazoline, 3,4,5-trimethoxyphenyl-2-imidazolines and tested for corrosion inhibition in 0.5M H$_2$SO$_4$ and 1M HCl using weight loss, Tafel polarization and electrochemical impedance techniques. Nalini et al found that the inhibition efficiency increased with the increase in concentration and higher efficiency of about 98% was obtained in both the acid media at 20 ppm. Adsorption obeys Langmuir adsorption isotherm and occurs spontaneously. Polarization curves reveal that it was a mixed type inhibitor.
Musa et al (2011 b) investigated the inhibition of mild steel corrosion in 2.5M H$_2$SO$_4$ solution by purpald (4-Amino-3-hydrazino-5-mercapto-1,2,4-triazole, 4-Amino-5-hydrazino-1,2,4-triazole-3-thiol) at 30ºC. Results showed that purpald performed as an excellent inhibitor for mild steel corrosion and it attained an efficiency of more than 95% at 4x10$^{-4}$ M. The inhibition efficiency increases with an increase in the concentration of purpald. Polarization curves show that it was a mixed type inhibitor.

Cefixime, a drug was studied for its corrosion inhibition on mild steel in acidic media. The results obtained divulged that this pharmaceutical compound had established > 90% inhibition efficiency at an optimum concentration of 8.8 x 10$^{-4}$ M. The outcomes show that inhibition takes place by adsorption of the inhibitor on metal surface without altering the mechanism of corrosion process and adsorption takes place according Langmuir’s adsorption isotherm. Cefixime acts as a mixed type of inhibitor (Imran Naqvi et al 2011).

Kumaravel et al (2011) studied the corrosion inhibition efficiency of a newly synthesized Schiff’s base for the corrosion of mild steel in 1M HCl and 0.5M H$_2$SO$_4$ solutions. Maximum efficiency was observed at an optimum concentration of 600 mg/l. It acted as a mixed type of inhibitor with properties more cathodic in nature. The adsorption followed Langmuir adsorption in both the acid media. The negative values of $\Delta G_{ads}$ indicated adsorption to be spontaneous.

A newly synthesized glycine derivative was used to control mild steel corrosion in 4M H$_2$SO$_4$ solutions at different temperatures. Tafel polarization measurements revealed that the inhibitors function as mixed-type compounds. The inhibition efficiency increased with increase in inhibitor concentration and decreased with increase in temperature, suggesting the
occurrence of physical adsorption. The adsorptive behaviour followed Temkin-type isotherm (Amin and Ibrahim 2011).

Deng et al (2011 a) studied the inhibition effect of acid violet 6B on the corrosion of cold rolled steel in 1.5M HCl solution. The results showed that acid violet 6B obeyed Langmuir adsorption isotherm and it behaved as a mixed-type inhibitor. EIS spectra exhibited an capacitive loop and confirmed the inhibitive ability.

Singh and Quraishi (2011) reported the corrosion inhibition properties of disulfiram for mild steel in HCl solution. Physical adsorption was proposed for the inhibition and the process followed the Langmuir adsorption isotherm and kinetic/thermodynamic model of El-Awady et al. The use of inductive element significantly improved the quality of fit of simulation to the EIS data.

Wang et al (2011) showed the influence of benzimidazole derivatives as corrosion inhibitor of mild steel in different concentrations of HCl solutions. The results suggested that the derivatives acted as a mixed-type inhibitor via strong chemical adsorption onto mild steel surface to suppress simultaneously both anodic and cathodic processes according to the Langmuir adsorption isotherm. Inhibition efficiencies increased with increasing concentration of the inhibitor and HCl.

Kesavan et al (2012) in their review briefly discussed some of the interesting features of the green inhibitors reported during the last decade. They concluded that green inhibitors are excellent inhibitors under a variety of corrosive environments for most of the metals. The non-toxicity and biodegradability are the major advantages for these inhibitors and further research efforts are needed to employ the green inhibitors widely at an industrial level.
1.24.2 Studies related to Corrosion Inhibition of Mild Steel by Plant Extracts in Hydrochloric Acid

The inhibitive effect of *Citrus Paradisi* (Grape fruit) on the corrosion of mild steel in HCl was reported by Olusegun et al (2004) using weight loss technique in the temperature range of 30ºC to 50ºC. The inhibitor efficiency increased with increase in inhibitor concentration but decreased with an increase in temperature.

*Prunus cerasus* juice inhibition effects on the corrosion of steel in hydrochloric acid solution were investigated using polarization and electrochemical impedance techniques. Corrosion inhibition increased as its concentration increased. Inhibition was attributed to adsorption of the phytochemical compounds in this juice. The reduction of corrosion inhibition efficiency by increasing the temperature may be due to thermal degradation of its organic content especially degradation of anthocyanine pigments (Ashassi-Sorkhabi and Seifzadeh 2006).

Afidah Rahim (2007) studied the inhibitive effect of Mangrove tannins and their flavonoid monomers on the corrosion of mild steel in aerated HCl by electrochemical methods. The monomers were found to be mainly cathodic inhibitors and the inhibition efficiency was dependent on concentration. The inhibitive performance of mangrove tannins was comparable to the other tannins investigated indicating their potential in corrosion protection.

Raja and Sethuraman (2008 a) reported the inhibitive effect of natural products on the corrosion of metals and alloys in corrosive media. Large numbers of organic compounds were studied and are being studied to investigate their corrosion inhibition potential. This study gave a vivid
account of natural products which are used as corrosion inhibitors for various metals and alloys in aggressive media.

Poongothai et al (2009 b) studied the corrosion inhibiting effect of five essential oils on the steel in hydrochloric acid environments using weight loss and polarization methods. In both methods, maximum inhibition efficiency was observed at 4% concentration of the inhibitors. Stevenson chamber tests showed that vapour phase corrosion inhibitors (VCI) offers corrosion inhibition efficiency up to 90% for mild steel. Electrochemical polarization studies suggested VCI as a mixed type inhibitor.

The inhibitive effect of acid extract of *Myristica Frangans* on mild steel in 1M HCl by weight loss, D.C polarization method and A.C impedance spectroscopy was investigated by Karthikaiselvi et al (2009). Results indicated that inhibition efficiency increased with increase in inhibitor concentration and with temperature. The adsorption followed Langmuir adsorption isotherm. Electrochemical measurements revealed that the extract act as a mixed type inhibitor.

Vasudha and Saratha (2007) studied the inhibition efficiency of acid extract of dry seeds of *Erythrina Suberosa* as corrosion inhibitor for mild steel in HCl medium. Experimental methods included weightloss and polarization studies. The results indicated as high as 98% at 1% inhibitor concentration. Adsorption isotherm reveal that it obeyed Temkin, Freunlich, Langmuir and Flory- Huggins isotherms.

The corrosion inhibition of mild steel in HCl solution by black pepper extract was studied by Quraishi et al (2009). The results obtained revealed a maximum efficiency of 98% at 120 ppm at 35°C. Potentiodynamic polarization curves showed that black pepper extract was a mixed type inhibitor. Adsorption of the inhibitor on the mild steel surface followed
Langmuir adsorption isotherm. The free energy of adsorption $\Delta G_{ads}$ indicated chemisorptions.

Due to ease of application, cost efficiencies and environmental safety, the corrosion inhibition effect of aqueous extract of *Eclipta Alba* in 1N hydrochloric acid was investigated. Shyamala and Arulanantham (2009) studied the effect of immersion time and temperature and results revealed that with an optimum concentration of 8.0% v/v showed a maximum inhibition efficiency of 99.6% at 3h immersion time and 30ºC Polarization studies indicated that this plant extract act as a mixed type inhibitor.

The inhibitive action of henna extract (*Lawsonia inermis*) and its main constituents (lawsone, gallic acid, $\alpha$-D glucose and tannic acid) on corrosion of mild steel was investigated. Polarization measurements indicated that all the examined compounds act as mixed inhibitor and inhibition efficiency increased with inhibitor concentration. Inhibition efficiency increased in the order lawsone > henna extract > gallic acid > glucose > tannic acid (Ostovari et al 2009).

Investigation of corrosion inhibition effect of black pepper extract and its piperine isolated from (BP) on corrosion of C38 steel in 1M HCl solution showed that the natural compounds tested exhibit higher efficiency exceeding 95% and 2 g/L. The presence of piperine decreased hugely the corrosion rate and its inhibition efficiency increased with concentration to attain 99% at $10^{-3}$M (Dahmani et al 2010).

Poongothai et al (2010 a) studied the corrosion vapour inhibition efficiency of five essential oils on mild steel in sea water, rain water, sulphur dioxide and hydrogen sulphide environments by weight loss and electrochemical methods. The highest inhibition efficiency was observed in all the tests at an inhibitor concentration of 4%. The tests also indicated that
the five oils act as mixed inhibitors but cathodic inhibition was more predominant.

Corrosion inhibition effect of acid extract of the pericarp of the fruit *Garcinia Mangostana* on mild steel in hydrochloric acid was studied. Study reveal that corrosion inhibitor efficiency of the extract increased with increase in inhibitor dosage and decreased as the temperature was raised. Electrochemical parameters indicated the mixed mode of inhibition but predominantly cathodic. Vinod Kumar et al (2010) indicated that the adsorption on the metal surface was due to heteroatoms present in the organic constituents of the extract.

The inhibitive action of extract of curry leaves (*Murraya Koenigii*) on carbon steel in 1N HCl was studied. The maximum inhibition efficiency was found to be 84.6% at an optimum concentration of 4% in v/v of the extract. Potentiodynamic polarization studies indicated that it was mixed type inhibitor and followed Langmuir adsorption isotherm (Sharmila et al 2010).

The inhibitive action of the aqueous extracts of fruit peels against corrosion of carbon steel in 1M HCl solution was investigated by Janaina et al (2010). The aqueous extract of mango, orange, passion fruit and cashew peels in different concentration were found to act as good corrosion inhibitor for the tested system. The inhibition efficiency increased with increasing extracts concentration and decreased with temperature. The adsorption of components of the fruit peel extracts on the surface of the carbon steel followed the Langmuir adsorption isotherm.

Ambrish singh et al (2010) evaluated the inhibition of the corrosion of mild steel in hydrochloric acid solution by the extract of Kalmegh (*Andrographis paniculata*) leaves extracts. Inhibition was found to increase with increasing concentration of the extract. The inhibition was assumed to
occur via adsorption of the inhibitor molecules on the metal surface which obeyed Langmuir adsorption isotherm.

Cathodic and anodic polarization curves showed that *Oxandra asbeckii* plant was a mixed type inhibitor on the corrosions of C 38 steel in 1N HCl and its inhibition efficiency increased with the inhibitor concentration. The adsorption of the plant extract obeyed Langmuir adsorption isotherm (Lebrini 2011 b).

Gravimetric method was used to study the temperature effects on carbon steel corrosion in molar HCl solution, in the absence and presence of methanolic extract of *Euphorbia Falcata. L*. The results revealed that the inhibition efficiency increased with inhibitor concentration, highest being 96% at 323 K at 3 g/L. The adsorption was spontaneous and followed Langmuir adsorption isotherm at all studied temperature (El bribri et al 2011).

Corrosion inhibition effect of alkaloid extracts from *Palicourea guianensis* plant on C38 steel in 1M HCl medium was studied by Lebrini et al (2011a). Polarization studies showed that the plant extract acts as mixed type inhibitor. Inhibition efficiency of 98% was achieved with 100 mgL$^{-1}$ of the extract at 25ºC.

Loto et al (2011 b) at the ambient working temperature studied the best corrosion inhibition performance for mild steel using the solution extracts of tobacco at 100% concentration in 0.5M HCl. The use of tobacco for the inhibition of corrosion of mild steel in this acid proved very effective with an average inhibitor efficiency of 96.25%. Kola leaf had a very fairly good performance at 73.82% inhibitor efficiency and kola nut had 78.60%.
1.24.3 Studies related to Corrosion Inhibition of Mild Steel by Plant Extracts in Sulphuric Acid

Inhibitive and adsorption properties of *Orphenadrine* for the corrosion of mild steel in 2.5M H$_2$SO$_4$ have been studied using hydrogen evolution and thermometric methods. Inhibition efficiency was found to increase with increase in concentration but decreased with increase in temperature. Calculated values of enthalpy and free energy change revealed that adsorption was exothermic and spontaneous. Based on values of activation energy and free energy of adsorption, Ekop et al (2008) proposed a physical adsorption mechanism.

Patel et al (2009) discussed the corrosion inhibition extract of *Bauhinia purpurea* leaves on mild steel 1N H$_2$SO$_4$ using conventional weightloss, electrochemical polarization, electrochemical impedance spectroscopy and scanning electron microscopic studies. The results show that inhibition efficiency of the extract increased gradually with increase in its concentration and attained a maximum value of 96% at 200 ppm and decreased marginally with rise of the temperature.

Odiongenyi et al (2009) studied the inhibitive and adsorption properties of ethanol extract of *Vernonia Amygdalina* for the corrosion of mild steel. The inhibition efficiency of the extract increased as the concentration of the extract increases. Phytochemical studies revealed that ethanol extract of *Vernonia amygdalina* contains tannins, saponins, flavonoids and anthraquinones which contribute to the corrosion inhibition through physical adsorption mechanism.

Saratha et al (2009) tailored the efficiency of acid extract of dry *Nyctanthes arboristris* (Night Jasmine, Coral Jasmine) leaves as corrosion inhibitor for mild steel in 1N H$_2$SO$_4$ medium. Experimental methods included
weight loss and polarization studies. The results indicated that the leaves extract were a good corrosion inhibitor and was of a mixed type, having efficiency as high as 90% at 1% inhibitor concentration.

Ekpe et al (2010) studied the inhibitive action of leaves, root and seeds extracts of *Azadirachta indica* on mild steel corrosion in sulphuric acid solutions using weight loss and gasometric techniques. Inhibition efficiency was found to increase with extracts concentration and temperature. A mechanism of chemical adsorption of the phytochemical components of the extracts on the surface of the metal was proposed. The experimental data fitted into Freundlich adsorption isotherm.

Bakery waste-egg shell extract was tested for its inhibitor effect towards mild steel in 0.5M H$_2$SO$_4$ solution. Temperature studies were conducted to evaluate the kinetic and thermodynamic parameters. Experimental results were fitted into various adsorption isotherms. Tafel polarization studies revealed the mixed mode of inhibition. Rajalakshmi et al (2010 b) suggest that egg shell serve as an effective zero cost, environmentally friendly inhibitor.

Based on the fact that one of the most important features of corrosion scaling inhibition products was the ability to stop oxidative processes. Pirvu et al (2010) studied the chemical characterization of some whole and selective vegetal extracts with high antioxidant activity isolated from *Fagus sylvatica* leaves and *Alii cepae bulbus* scales raw materials. Chemiluminescence measurements revealed strong antioxidant activities, ranging from 73% to 95%. Corrosion / scaling inhibition tests confirmed both onion scales extract’s superiority as well as selective extract’s effectiveness.

The inhibition efficiency of acid extract of leaves of *Emblica officinalis* plant on the corrosion of mild steel in 0.5M H$_2$SO$_4$ was confirmed
by gasometrical studies. Studies revealed that the adsorption of the phytochemical constituent on the surface of mild steel was spontaneous via the mechanism of physical adsorption and followed the Langmuir, Temkin, Freundlich adsorption isotherms. The extract was found to be stable at room temperature and showed an efficiency up to 97.23% (Saratha et al 2011 b).

The corrosion inhibition effect of extracts of kola plant (Cola acuminata) and green tea (Camellia sinensis) in mixed form on the protection of mild steel specimens immersed in sulphuric acid solution was studied. Loto et al (2012 a) found that the extracts of kola plant and green tea in different concentrations and combinations were used as ‘green’ inhibitors. The best corrosion inhibition performance for mild steel was obtained at 100% concentration.

### 1.24.4 Studies related to Corrosion Inhibition of Mild Steel by Plant Extracts in Hydrochloric and Sulphuric Acid

Noor (2007) reported the inhibition efficiencies of Fenugreek leaves and seeds on mild steel corrosion in acidic solutions. Results revealed that in both HCl and H\textsubscript{2}SO\textsubscript{4} the extracts acted as anodic type inhibitors. Efficiency increased with increase in concentration and efficiency was found to be greater in HCl than in H\textsubscript{2}SO\textsubscript{4} solutions. In HCl solution the adsorption obeyed the Langmuir isotherm while in H\textsubscript{2}SO\textsubscript{4} it obeyed the Temkin isotherm.

Okafor et al (2008) studied the inhibitive effect of Phyllanthus amarus extract on the corrosion of mild steel in HCl and H\textsubscript{2}SO\textsubscript{4} by weight loss and gasometric techniques. The results indicate that the extracts functioned as a good inhibitor in both the environment and inhibition efficiency increased with extracts concentration. Temperature studies revealed an increase in inhibition efficiency with rise in temperature and decrease in
the activation energies in the presence of the extract. The adsorption characteristics of the inhibitor were approximated by Temkin isotherm.

Oguzie (2008) studied inhibitive effect of *Hibiscus sabdariffa* extract on the corrosion of mild steel in 1M H₂SO₄ and 2M HCl by gasometric technique. The results demonstrate that Hibiscus sabdariffa extract suppressed the corrosion reaction in both acid media inhibitor with slightly higher values obtained in 1M H₂SO₄. Synergistic effects increased the efficiency of the extract in the presence of halide additives. Adsorption characteristics of the extract were approximated by the Langmuir isotherm.

Acid extract of *Solanum Tuberosum* was tested as corrosion inhibitor for mild steel in 1M HCl and H₂SO₄ media using different techniques. Tafel polarization indicated that the plant extract behaves as a mixed mode inhibitor. Increase of inhibition efficiency with increase of temperature along with Eₐ values serve as a proof for chemisorptions (Raja and Sethuraman 2009 b).

Abdel-Gaber et al (2009) observed the effect of lupine (*Lupinus albus L.*) extract on the corrosion of steel in aqueous solution of 1M sulphuric acid and 2M hydrochloric acids. Potentiodynamic polarization curves indicated mixed type inhibition and efficiency was found to increase with increasing concentration of the extract.

*Adhatoda vasica* acted as good inhibitor in HCl, H₂SO₄ and H₃PO₄ for mild corrosion. It was found to contain alkaloids. Corrosion rate decreased with increase in concentration of inhibitor. Maximum inhibition efficiency was obtained for 1N HCl (1h) = 77.77%. In this investigation the extract acted as a good inhibitor in HCl than, H₂SO₄ and H₃PO₄. From the potentiostatic polarization studies curves, the extract acted as mixed type inhibitor (Matheswaran et al 2010).
The inhibitive efficiency of an aqueous extract of *Tridax procumbens* L. in controlling corrosion of mild steel has been investigated by weight loss method in the absence and presence of corrosion inhibitor at different time interval at room temperature. The result showed that the corrosion inhibition efficiency of these compounds varied with different time interval and different acid concentration. The corrosion behaviour of *Tridax procumbens* L. was greater in sulphuric acid than in hydrochloric acid medium (Ilayaraja et al 2011).

The inhibitive effect and adsorption properties of petiole extract obtained from destructive distillation of *Cocos nucifera* for the corrosion of mild steel in 0.5M H\(_2\)SO\(_4\) and 1M HCl was investigated by Vijayalakshmi et al (2011). Values of Tafel constant \(b_a\) and \(b_c\) confirm that the coconut palm petiole extract acts like mixed type inhibitor. The adsorption of the inhibitor on mild steel surface was found to be spontaneous, endothermic and consistent with the assumptions of Langmuir adsorption isotherm.

### 1.24.5 Studies related to Corrosion Inhibition of Mild Steel by Plant Extracts in Phosphoric Acid

The inhibition effect of *Zenthoxyllum alatum* plant extract on the corrosion of mild steel in 20, 50 and 88% aqueous orthophosphoric acid was studied by Gunasekaran et al (2004). Plant extract was able to reduce the corrosion of steel more effectively in 88% phosphoric acid than in 20% phosphoric acid. The effect of temperature on the corrosion behaviour of mild steel in 20, 50 and 88% phosphoric acid with addition of plant extract was studied in the temperature range 50ºC-80ºC. Results on corrosion rate and inhibition efficiency indicated that this extract was effective up to 70ºC in 88% phosphoric acid medium.
Ghanbari et al (2009) studied the corrosion inhibition performance of acetylacetonate complexes of zinc (II), manganese (II), cobalt (II) and copper (II) on the mild steel substrate in 1M H$_3$PO$_4$. The potential of mild steel shifted towards more potentials. The cathodic Tafel slopes increased showing that the complexes are cathodic inhibitors. Presence of chloride ions in the electrolyte enhanced inhibition performance. Chloride ions provided by HCl had a better performance compared to NaCl.

Sivaraju and Kanann (2010) studied the inhibition effect of *Acalypha indica L.* alcoholic extract on mild steel corrosion in 1N phosphoric acid. The inhibition efficiency increased with increase in concentration. The corrosion rate increased with increase in temperature and decreased with increase in concentration of inhibitor compared to blank. The adsorption of inhibitor on mild steel surface was found to obey Temkin’s adsorption isotherm.

The corrosion inhibition of 3-amino-1,2,3-triazole on the mild steel in phosphoric acid solution was found to increase with concentration and was found to act as a mixed type inhibitor (Malki Alaoui et al 2011). It also retarded the cathodic reaction by changing the mechanism of the hydrogen evolution reaction.

1.24.6 Studies related to Corrosion Inhibition of other Metals in Various Corrosion Inhibitors using Different Media

Extracts of *Ricinus communis* leaves were tested for corrosion inhibitory effect towards mild steel in 100 ppm sodium chloride solution by Ananda Louise Sathiyanathan et al (2005). It was found from weight loss measurements that the corrosion inhibition efficiency was about 84% in 300 ppm of the plant extract. Polarization measurements indicated that the plant extract acted as anodic inhibitor. Electrochemical impedance results showed
that the plant extract increased the corrosion resistance and the formation of iron-organic complex reduced the corrosion in neutral system.

Umoru et al (2006) investigated the inhibitive effect of cocoa and kolanut extracts on the corrosion of mild steel in seawater. The results showed potential inhibition of mild steel corrosion in seawater and marine environment. The highest inhibition efficiency was obtained when the concentration of the inhibitors was increased up to optimum. There was a sign of synergism when 4% of each of the extract were used to inhibit corrosion in the sea water.

The inhibitive effect of the gum exudates from *Acacia seyal* var. *seyal* on the corrosion of mild steel in drinking water was investigated using potentiodynamic polarization and electrochemical impedance techniques. The results obtained by Buchweishaija and Mhinzi (2008) showed that gum exudates behave predominantly as an anodic inhibitor and the inhibition efficiency was insignificantly affected by the temperature rise of the medium.

Osarolube et al (2008) reported the corrosion behavior of mild steel and high carbon steel in various concentrations of nitric acid, hydrochloric acid and perchloric acid. It was observed that nitric acid environment was most corrosive both to steels because of its oxidizing nature, followed by perchloric acid and lastly, hydrochloric acid. The corrosive concentration and exposure time affected the corrosion of the metal. Corrosion rates of mild steel in all the acidic media studied were found to be higher than that of high carbon steel. This could be attributed to the fact that the carbon content in itself had little effect on general corrosion resistance of steel.

The inhibition efficiency of an aqueous extract of beet root in controlling corrosion of carbon steel in well water in the absence and presence of Zn$^{2+}$ was evaluated. Polarization studies revealed that the formulation
controls the cathodic reaction. AC impedance spectra revealed the formation of protective film on the metal surface. FTIR spectra reveal that the protective film consists of Fe$^{2+}$ - betanin complex and Zn(OH)$_2$. The film was found to be UV-fluorescent (Arockia Selvi 2009).

Atmosphere corrosion rate of Al, Zn and mild steel as well as salinity and sulphation rate was determined under outdoor exposure. Mild steel samples exposed vertically suffered less corrosion than those exposed at an angle 45º. Vashi and Kadiya (2009) observed that the monthly corrosion rate was in the decreasing order of Al < Zn < MS. The yearly rate also followed the same trend.

Nnanna et al (2010 b) investigated the corrosion inhibition of aluminium alloy in 0.5M HCl by extracts of selected plants like Euphorbia hirta and Dialum guineense. The results indicated that all the extracts inhibited the corrosion process in the medium by the virtue of adsorption and inhibition efficiency improved with concentration. Inhibition mechanism were deduced from the temperature dependence of the inhibition efficiency as well as from activation parameters that govern the process.

The inhibition of the corrosion of mild steel in aqueous solutions by ethyl acetate extract of Uncaria gambir containing catechin was investigated. Inhibition was found to be highest at a concentration of 150 ppm in solutions with a pH of 5. The results showed that the extract act as a mixed type inhibitor and could serve as an effective inhibitor (Hussin 2010).

The inhibitor property of Piper nigrum Linn. seeds for acid corrosion of aluminium alloy (AA1100) was investigated by Rekha Nair et al (2010). Kinetic and adsorption parameters were calculated. The inhibition efficiency was found to increase with increase in inhibitor concentration. The experimental data were fit into the El-Awady’s thermodynamic-kinetic
model. Surface analysis was carried out by FTIR to ascertain the anti-corrosive property of the inhibitor.

The inhibition efficacy of *Punica granatum* extract on the corrosion of brass in 1N HCl was studied. The inhibition efficiency increased with increase of inhibitor concentration but decreased with rise in temperature and time. Based on the values of activation energy, free energy of adsorption and variation of inhibition efficiency with temperature, Deepa rani and Selvaraj (2010) proposed a physical adsorption mechanism for the adsorption.

The corrosion inhibition efficiency of carbon steel pipelines in 1M HCl by the synthesized novel surfactants was studied. Hegazy et al (2011) reported that the inhibition efficiencies of all the synthesized inhibitors increased with increase in both concentration and temperature. It was influenced by the type of the functional groups substituted on the benzene ring. Polarization curves revealed that the studied inhibitors represent a mixed type of inhibitors.

The inhibition effect of tetradecylpyridinium bromide on the corrosion of aluminium in 1.0M HCl solution was found to obey Langmuir adsorption isotherm. Polarization curves reveal that it behaved as a cathodic inhibitor. Li et al (2011) observed that EIS spectra consist of large capacitive loop at high frequencies followed by a large inductive one at a low frequency values which confirm the inhibitive ability.

Deng et al (2011 b) synthesized two pyrazine derivatives of 2-aminopyrazine (AP) and 2-amino-5-bromopyrazine (ABP) and studied the inhibition effect on the corrosion of cold rolled steel in 1.0M HCl. Inhibition efficiency followed the order ABP > AP. Adsorption obeyed Langmuir adsorption isotherm. The two pyrazine derivatives act as mixed inhibitors.
Nwabanne and Okafor (2011) investigated the inhibitive, thermodynamic and adsorptive properties of ethanol extract of *Vernonia amygdalina* for the corrosion of mild steel in 0.4M HNO$_3$ solutions. The inhibition capacity of this extract was attributed to the presence of saponins, tannins, alkaloids, anthroquinones, flavanoids, cardiac glycosides in the extract. The heat of adsorption obtained indicated that adsorption on the surface of mild steel was exothermic, spontaneous and followed the mechanism of physical adsorption. Langmuir, Temkin, Frumkin and Flory-Huggins adsorption isotherms were found to confirm the adsorption characteristics of the inhibitor.

The inhibitive effect of leaf extract of *Euphorbia hirta* on aluminium corrosion in HCl and NaOH solutions were studied. Nnanna et al (2011 a) found that the leaf extracts of *E. hirta* demonstrated better inhibition efficiency in the acidic medium than in alkaline medium. Physical adsorption mechanism was proposed from the obtained thermodynamic parameters.

The inhibitive effect of hydroxyethylcellulose on mild steel and aluminium corrosion in 0.5M HCl solution under atmospheric exposure was observed. From the results obtained Arukalam et al (2011) observed that the corrosion rate was higher in aluminium than in mild steel. Inhibition efficiency and surface coverage were however, found to be higher in mild steel than in aluminium. In addition, corrosion current was determined and was found to be higher in mild steel in aluminium.

Nwigbo et al (2011) explored the possibility of using a typical plant extract other than the use of conventional materials as corrosion inhibitor. *Elaeis guineensis* exudates (Palm wine), was found to contain carbonyl groups, double bonds and triple bonds. The kinetics result showed that activation energy increased as temperature and inhibitor concentration increased.
Sangeetha et al (2011) made an elaborate overview on green corrosion inhibitors. To replace the environmentally hazardous chromates, several non-chromates have been used as corrosion inhibitors. Extracts of plant materials top the list. The plant extract are environmentally friendly, non-toxic and readily available. These extracts contain many ingredients. They contain several organic compounds which have polar atoms such as O, N, P and S. They are adsorbed onto the metal surface through these polar atoms and form a protective film. Adsorption of these ingredients obey various adsorption isotherms. The films have been analyzed by many surface analysis techniques such as AFM, FTIR, UV, Fluorescence spectra and SEM.

The effect of *Citrullus Vulgaris* peel on the corrosion of zinc in natural sea water was studied by Petchiammal et al (2012). The percentage of inhibition efficiency increased with increase of inhibitor concentration and decreased with rise in period contact. The observed results concluded that the peel extract could serve as an effective inhibitor on zinc in natural sea water environment.

1.24.7 Studies related to Chemical Composition and Properties of Bananas

The phytocomponents present in banana peel was analyzed by Knapp and Nicholas (1969). The following sterols and triterpenes have been identified in banana peel: \( \beta \)-sitosterol, stigmasterol, campesterol, cycloeucalenol, cycloartenol, and 24-methylene cycloartanol, 24-methylene cycloartanol palmitate and an unidentified triterpene ketone were the major constituents. The ester represented approximately 30% of the total extractable lipid.
The occurrence of flavonoids in plants and their biochemical activities was studied by Julia Peterson and Johanna Dwyer (1998). Flavonoids are plant phytochemicals that cannot be synthesized by humans. The six classes of flavonoids (flavonones, flavones, falvonols, isoflavonoids, anthocyanins and flavans) vary in their structural characteristics around the heterocyclic oxygen ring. Flavonones occur predominantly in citrus fruits, flavones in herbs, isoﬂavonoids in legumes, anthocyanins and cataechins in fruits and flavonols in all fruits and vegetables.

The antioxidant compounds from bananas (*Musa Cavendish*) was isolated and it was found that Gallocatechin was more abundant in peel (158 mg /100 g dry weight) and was separated using HPLC which showed stronger antioxidant activity than that of the banana pulp extract (Someya et al 2002).

A correlation was established between production of specific phenylphenalenones and resistance of various banana and plantain varieties towards certain pathogens. (Otalvaro 2002). This compound was considered as a key intermediate in biosynthesis of phenylphenalenones phytoalexins.

Forster et al (2003) reported the chemical composition in the different parts of banana plant. The central part of banana pulp was the richest in nutrients, except for ascorbic acid.

Mokbel and Hashinaga (2005) studied antioxidant activity of banana fruit peel using the thiocyanate method, β-carotene bleaching method and 1,1-diphenyl-2-picrylhydrazyl method (DPPH) and antimicrobial activities of the extracts using paper disc methods and minimum inhibition concentration (MIC). The ethyl acetate and water soluble fractions of green peel displayed high antimicrobial and antioxidant activity respectively. Antioxidant activity of water extracts was comparable to those of synthetic antioxidants.
Emaga et al (2007 a) studied the chemical composition of six varieties of fruit peels of the banana and plantain. The protein content in peel of the banana and plantain was 8-11%. Leucine, valine, phenylalanine and threonine were essential amino acids in significant quantities. The content of lipid varied from 2.2% to 10.9% and was rich in polyunsaturated fatty acids particularly linoleic acid and α-linolenic acid.

Anhwange (2008) analysed *Musa sapientum* (Banana) peels for minerals, nutritional and anti-nutritional contents. The percentage concentration of protein, crude lipid, carbohydrate and crude fiber were 1.70, 59.00 and 31.70 respectively. The study of the anti-nutrient content of the peels generally indicated low values except saponins.

Maisuthisakul et al (2008) studied antioxidant capacity of plants. The results showed that plants which are rich in phenolic components are of interest as source of natural antioxidants and many plant components can act as antioxidants. Antioxidant activity correlated well with phenolic and flavonoid contents.

Sheng et al (2010) compared the nutritional composition of two cultivars. The results indicated that banana flowers are good source of minerals such as magnesium, iron and copper. It contains high quality protein because of its well balanced essential amino acid in addition to high dietary fibre and flavonoid concentrations. The contents of Vitamin E, total saponin and flavonoids were 0.87, 0.12 and 5.27 mg/100 g, respectively. The results also confirmed that higher flavonoids were present in banana flower than in banana peel.

The antioxidant capacity and phenolic content of different solvent extracts from banana (*Musa paradisiaca*) was studied extensively by
Loganayaki et al (2010). Chloroform, acetone and methanol extracts from stem and flower of banana were evaluated for their invitro antioxidant activity using ferric reducing antioxidant power (FRAP), 2,2-diphenyl-1-picryl-hydrazyl (DPPH), 2,2’azinobis (3-ethyl benzothiazoline-6-sulphonic acid) diammonium salt (ABTS), iron chelation and antihemolytic activity. The results showed that the total phenolic content was higher in these extracts and the antioxidant potential of the extracts was well established. The potential of multiple antioxidant activity of samples can be further evidenced by inhibition of reactive oxygen mediated erythrocyte cell lysis and metal ion chelating activity.

Banana (Musa acuminate Colla AAA) peel extracts were to be good lipid peroxidation inhibitors. Banana peel contained large amounts of dopamine and L-dopa, catecholamines with a significant antioxidant activity (Montelongo et al 2010). The antioxidant activity of banana peel extracts from different cultivars was similar.

Mohapatra et al (2010) discussed the usefulness of banana fruits, peel, leaves pseudostem, sheath, pith and male bud and prospects of using these materials in industry. Banana plant parts are useful as insecticide, antioxidant, colour absorber, in the preparation of various functional foods, wine, alcohol, biogas, cattle feed etc. Bananas are rich in phenolic compounds and flavonoids, which have antioxidant properties. Bananas are rich in dopamine, an antioxidant. Chemical constituents of banana were investigated by means of chromatographic techniques.

A natural product of the phenylphenalenone type, 3-hydroxy-4-phenyl-1H,3H-benzo[de]isochromen-1-one and two known natural products, methoxyanigorufone and isoanigorufone were isolated and identified by NMR
spectroscopy and mass spectroscopy. Additionally, by HPLC analysis, three
dimeric phenylphenlenones, namely anigorootin, \(4',4''\)-dihydroxyyanigorootin,
were identified by Jitsaeng et al (2010).

The phytochemical constituents and antioxidant activities of banana
flower of *Musa x paradisiaca* was reported by Mahmood et al (2011). Phytochemical studies on banana flower extracts showed the presence of
alkaloids, glycosides, steroids, saponins, tannins, flavonoids and terpenoids.
Study showed that banana flower contained crude chemical constituents of
tannins (7.83%), flavonoids (0.16%), saponins (1.43%), alkaloids (1.56%)
and total phenolic compounds (2.98%). The study also showed potent
antioxidant activity in banana flower, of which the ethanol extract
demonstrated much stronger activity than water extract with the \(IC_{50}\) value of
29.75 µg/ml and 1.52 mg/ml, respectively.

The bioactivity and phytochemical screening of *Musa acuminata*
flower was performed by Sumathy et al (2011). The flower extract showed
good antimicrobial activity. The antioxidant study revealed that the flower
was a good antioxidant source like butylated hydroxytoluene (BHT) with
\(LC_{50}\) values of 7.83 mg/ml. Phytochemical screening confirmed the presence
of active compounds like glycoside, tannins, saponins, phenols, steroids and
flavoids in the *M. acuminata* flower metabolic extracts.

Ghosh et al (2011) studied the importance and enormous
pharmacological action of different variety of Musa species. The family
*Musaceae* having 2 genera and 42 different species and within 42 species, 35
species belongs to Musa species. Different chemical constituents like Isoamyl
acetate, 2-heptylacetate, 2-methyl butyl acetate, 2-heptyl hexanoate, 3-
hydroxy-4-phenyl-1H,3H-benzo[de]isochromen-1-one, Methoxy anigorufone
are present. Musa species are having a number of valuable pharmacological activities like ulcer protective activity, antibacterial activity, wound healing activity, antioxidant activity and mutagenic effect. Different Musa species are used for different purpose for their particular individual features. The pharmacological effects of Musa species might be a target for the researcher for the development of less toxic components.

Six different cultivars of banana flowers (Musa paradicicus) (Kathali, Bichim Shingpuri, Kacha, Champa and Kalabou) were analysed by Ratna china et al (2011) for the content of polyphenol expressed as gallic acid equivalent and flavonoid expressed as quercetine equivalent and the in vitro total antioxidative activities of the flower extracts. Hepatic cell damage in iron-mediated Fenton reaction caused by free radicals was reduced by the banana flower extract. On the basis of the results obtained, the banana flowers were found to be potential source of antioxidants.

Shyamala and Jamuna Prakash (2011) made a comparative study of the chemical composition and antioxidant potential of peels of Pachabale, Yelakkibale and Nendran bale. A higher free radical scavenging activity (90%) was obtained in Nendran bale peel in ethanol extract. Among the three varieties Nendran bale peel exhibited high antioxidant activity. The antioxidant activity of peels could be correlated positively with polyphenols, flavonoids and tannins.

The influence of variety (Cavendish and Dream), stage of ripeness (green and ripe) and parts (pulp and peel) on antioxidative compounds and antioxidant activity of banana fruit was investigated. Fatemeh et al (2012) reported that total phenolic compound and total flavonoid compound values
of banana peel were higher than those of banana pulp. Also green banana showed higher TPC and TFC values than those of ripe fruit.

1.24.8 Studies related to Corrosion Inhibition of Mild Steel by Musa Species

Eddy and Ebseno (2008 a) reported the inhibition of the corrosion of mild steel by ethanol extract of Musa Sapientum peels in H₂SO₄ was studied using gasometric and thermometric methods. It was found that inhibitive action of M. Sapientum peels is basically controlled by temperature, pH, and period of immersion, electrode potential and concentration of the inhibition. Adsorption mechanism of the inhibitor follows physical adsorption mechanism.

Eddy et al (2009 d) studied the inhibition of corrosion of mild steel by ethanol extract of Musa species peel using hydrogen evolution and thermometric methods of monitoring corrosion. Inhibition efficiency of the extract was found to vary with concentration, temperature, period of immersion, pH and electrode potentials. Thermodynamic consideration revealed that the adsorption was spontaneous and occurred according to Langmuir and Frumkin adsorption isotherms. Physical adsorption mechanism has been proposed for the adsorption of the inhibitor.

The inhibitive properties of solid waste (Genus Musa-banana, Genus Saccharum-sugarcane and Citrullus Lanatus-watermelon) on corrosion of mild steel strip in 1M HCl were investigated using weight loss technique by Ismail et al (2011). Inhibition efficiency of 69.60%, 68.41% and 58.15% at 10% v/v of extracts concentration for 72 hours exposed time were achieved for Genus Saccharum, Citrullus lanatus and Genus Musa respectively. Adsorptions of the inhibitors molecules on mild steel strip surfaces were consistent with Langmuir adsorption isotherm.
The inhibition of copper corrosion by *Gnetum africana* and *Musa acuminate* peel under various concentrations of HNO₃ at different temperatures of 303 K and 333 K was studied by weight loss methods. For both extracts inhibition efficiency was found to increase with increase in extract concentration and decrease with increase in temperature and period of immersion. The inhibition efficiency of *Gnetum Africana* was greater than that of *Musa acuminate* peel for otherwise identical conditions. Values of activation energy of inhibited corrosion reaction of copper of both peel extracts were greater than the values obtained for the blank. Thermodynamic consideration revealed that adsorption of both inhibitors was spontaneous, physically controlled and occurred according to Langmuir adsorption isotherm (Ogbonna et al 2011).

The effect of extract of *Musa paradisiaca* on corrosion inhibition of mild steel in aqueous 0.5M sulphuric acid was investigated and results showed that inhibition occur via adsorption of inhibitor molecules on metals surface, which obeyed Langmuir adsorption isotherm (Mayanglambam et al 2011). The thermodynamic parameters indicated a strong interaction between the inhibitor and the mild steel surface.

Olasehinde et al (2012) studied the corrosion inhibition behaviour for mild steel by extracts of *Musa sapientum* peel in HCl solutions. The results showed that the corrosion rate decreased with increase in extract concentrations. Inhibition efficiency decreased with increase in temperature. Activation energy was found to be 61.60 kJ/mol for 1M HCl and increased to 66.72 kJ/mol in the presence of the peel extract. Kinetic studies revealed that it followed a first order reaction and the half life increased as the concentration of the extracts increased, suggesting that inhibition efficiency increases with increase in the concentration of the extract. Phytochemical
constituents showed that *Musa sapientum* contains tannin, flavonoid, terpenoid and some other compounds in trace constituents.

**1.25 SELECTION OF PLANT MATERIAL AS NATURAL CORROSION INHIBITOR**

Combining technological progress with environment safety has become a key challenge of the millennium. Large number of organic compounds used as corrosion inhibitors are not only expensive but toxic and non-biodegradable. There is growing need for green corrosion inhibitors which are eco-friendly, non-hazardous and bio-degradable. Wide range of inhibitors with rich sources of ingredients with high inhibition efficiency, environmentally acceptable, and readily renewable, do not contain heavy metals or toxic compounds.

Review of available literature shows that the selected plant materials have not been studied as acid corrosion inhibitors for mild steel and are available in plenty. The plant material and its various parts (Figure 1.5) used for studying the corrosive inhibitive nature on mild steel are given below,

Plant: *Musa acuminata* ‘Nendran’

<table>
<thead>
<tr>
<th>Part</th>
<th>MAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fruit peel</td>
<td>(P)</td>
</tr>
<tr>
<td>Flower</td>
<td>(F)</td>
</tr>
<tr>
<td>Bract</td>
<td>(B)</td>
</tr>
</tbody>
</table>
Figure 1.5 Photograph of *Musa acuminata* plant parts used as corrosion inhibitor

Figure 1.6 Photograph of *Musa acuminata* ‘Nendran’ cultivated farm
1.26 PLANT DESCRIPTION

1.26.1 Banana – General

Banana, an antique fruit crop of the world known as ‘Apple of the Paradise’ has played interesting and important roles in the history of human civilizations. This fruit is the food of sages since ancient time. The word banana is derived from the Arab word ‘banan’ which means finger. Banana belonging to the *Musaceae* family originated in the hot, tropical regions of south East Asia (Simmonds, 1962). Malaysia is considered as the primary centre of origin of *M. acuminata* and from there it spread to India and Burma.

*Musaceae* family has two genera and 42 different species and within 42 species, 32 species belongs to musa species (Nuengchamnong 2004).

Banana is an arborescent (tree like) perennial herb growing to height of 30 feet or more. Trunk like structure bears a crown of erect or arching paddle shaped leaves (Figure 1.6). A false stem pseudo stem is formed by the bases of the leaves. The shoot apex is present at the ground level. When matured, flowering structure that grows upward through the pseudo stem emerges at the top as a gigantic inflorescence (Figure 1.7). When flowering and fruit production are completed, the shoot dies, because the apex has been used up and new offsets are formed at the base of the plant on the corm. Thus, a plant can be productive upto ten years and the corm or suckers can be cut off and used to start new uplands by vegetative propagation. Vegetative propagation is essential because the plants never form seeds (Evans 2002).
1.26.2 Biological Evolution and Nomenclature of Banana Plant

Second largest produced fruit after citrus, contributing about 16% of the world’s total fruit production, the genus Musa, family *musaceae* comprises of bananas and plantains. They are large perennial herbs, growing from a sympodial rhizome. Edible bananas are derived from *Australimusa* and *Eumusa* series, which have different origins from same genus. Most of the edible bananas are either derived solely from *Musa acuminata* or are hybrid between two wide diploids species, *M. acuminata* Colla and *M. balbisiana* Colla which contributed to A and B genomes respectively. Various varieties exist naturally or developed by hybridisation of these genomes, which have different nomenclature. Three common species of Musa (*M. cavendishii*, *M. paradisiaca* and *M. sapientum*) are widely grown in the world. There is a great diversity of dessert bananas in terms of plant stature, fruit size and
colour. Most productive cultivars are Cavendish bananas and giant French plantains. Out of over 50 varieties of banana cultivated across India, 20 are commonly grown (Mohapatra et al 2010). They can be divided into different groups according to chromosome numbers and ploidy as well as characteristics contributed by two ancestors, *Musa acuminata* (genome type A) and *M. balbisiana* (genome type B) (Valmayor 1991). The banana nendran, which is a cultivar variety of *Musa acuminata*, is classified as AAB.

In banana, a large number of cultivars are available in India differing in several fruit characters and ecological trials. *Musa acuminata* also called as Nendran (AAB) is important in Kerala and Tamilnadu. Nendran is an important cooking bananas. Scientific classification of nendran banana is as follows,

- **Kingdom**: Plantae
- **Clade**: Angiospermae
- **Class**: Monocotyledones
- **Series**: Epigynae
- **Order**: Zingiberales
- **Family**: Musaceae (Banana)
- **Sub Family**: Scitamineae
- **Genus**: Musa
- **Species**: Musa acuminata
- **Cultivar variety**: Nendran
1.26.3 Composition and Uses

Banana is the most nourishing fruit, containing vitamins and minerals, and has several medicinal properties. It is a rich source of energy, low in protein and fat contents and provides a balanced diet. The composition of the fruit given by Simmonds (1966) is shown in Table 1.2.

Table 1.2 Composition of banana fruit

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
<th>Element</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>70.0</td>
<td>Phosphorus</td>
<td>290.0</td>
</tr>
<tr>
<td>Carbohydrate</td>
<td>27.0</td>
<td>Calcium</td>
<td>80.0</td>
</tr>
<tr>
<td>Crude fibre</td>
<td>0.5</td>
<td>Iron</td>
<td>6.0</td>
</tr>
<tr>
<td>Protein</td>
<td>1.2</td>
<td>β-carotene</td>
<td>0.5</td>
</tr>
<tr>
<td>Fat</td>
<td>0.3</td>
<td>Riboflavin</td>
<td>0.5</td>
</tr>
<tr>
<td>Ash</td>
<td>0.9</td>
<td>Niacin</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ascorbic acid</td>
<td>120.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Energy (Cal/100g)</td>
<td>104.0</td>
</tr>
</tbody>
</table>

The plant along with its fruit bunch is used extensively in all auspicious occasions such as weddings, festivals and for the worship of God. Fruits are used for table and culinary purposes. Central core of the pseudo stem and male bud are good for making delicious cuisines. Several processed products like chips, banana figs, soft drink, beer, wine, alcohol, vinegar, powder, jam, confectionaries and halwa are made from the fruit.

Banana leaf is considered as biological plate for serving dishes. Starch is manufactured from pseudo stem. Banana fibre from pseudo stem is
used for making carry bags. The sheaths and leaves are used for making crude ropes and wrapping materials. The plant parts can be used as a cattle feed.

Nutritive benefits of banana flower are: it is good source of vitamin C, vitamin A and vitamin B, potassium, magnesium, phosphorus, calcium and iron. In traditional medicine of India and the ancient Persia, this golden fruit was called as the ‘fruit of wise’ and regarded as nature’s secret of perpetual youth. All parts of the banana plant have medicinal applications. The flowers are used in treatment of bronchitis, constipation, ulcers and good for diabetics. Reduces painful and excess menstrual bleeding, enhance milk supply in lactating mothers. The astringent plant sap is used in the cases of hysteria, epilepsy, leprosy, fevers, haemorrhages, acute dysentery and diarrhoea. It is applied on haemorrhoids, insect and other stings and bites. Young leaves are placed as poultices on burns and other skin afflictions. The astringent ashes of the unripe peel and of the leaves are taken in for dysentery and diarrhoea and used for treating malignant ulcers. The roots are administered in digestive disorders, dysentery and other ailments. Banana seed mucilage is given in cases of catarrhea.

1.26.4 Banana Peel

The fruit of a banana is a berry with a leathery outer peel that contains much collenchyma. The banana - *Musa acuminata* ‘Nendran’, is a typical climacteric fruit made up of peel and edible pulp (Figure 1.8) and mainly grown in tropical and subtropical regions. Peel form about 18-33% of the whole fruit and are a waste product. Bananas are harvested green and keep ripening even after they are picked.
1.26.5 Banana flower

The inflorescence, a transformed growing point is a terminal spike shooting out from the heart in the tip of the stem. The word banana flower is variously translated as ‘banana blossom’, ‘banana heart’ due to its physical resemblance to that organ. At first, it is a large long-oval, tapering, and purple-clad bud (Figure 1.9). As it opens it is seen that the slim, nectar rich, tubular, toothed, white flowers are clustered in whorled double rows along the floral stack (Figure 1.10). Female flowers occupy the lower 5 to 15 rows; above them may be some rows of hermaphrodite or nectar flower. Male flowers are borne in the upper rows. Shortly after opening, the inflorescence begins to bend downward and the male flowers and bracts shed out leaving most of the upper stalk naked except at the very tip which remains unopened and contain last formed male flowers. The cut ends of the banana flower leak a sap that will stain skin and other surfaces black.
Figure 1.9  Photograph of inflorescence with floret and bract

Figure 1.10  Photograph of floret

1.26.6  Banana Bract

Each cluster of flower is covered by a thick, waxy, hood like bract, purple outside, deep red within (Figure 1.11). Bracts lift from the first hand in 3 to 10 days. The bracts are soon shed and fully grown fruits in each cluster become a hand of bananas.
Figure 1.11 Photograph of thick, waxy, hood like bract

1.27 CHARACTERIZATION OF PLANT MATERIAL

Musa species is one of the well known plants of the musaceae family that have been used in traditional medicine since hundred years to alleviate various disease and health problems. Active constituents present in the plant materials might be responsible for the benefit of human health. The most important of these bioactive components of plants are alkaloids, flavonoids, tannins and phenolic compounds (Atindehou et al 2002, Edeoga et al 2005) These compounds are well known to posses various bioactivities such as antioxidant, antimicrobial, antiviral and anticancer. Due to their potential to overcome health problems, plant based products have been produced in industries as botanical drugs, dietary supplements and functional foods. Recently most scientist have focused to investigate bioactive secondary metabolites in order to discover new medicinally and commercially important plant drugs.

Musa plant is known as the largest herbaceous flowering plant in the world. All the parts of banana plant are beneficial to mankind in the medicinal aspects and ornamental uses (Sumathy et al 2011). Ethnomedicinal survey around the world revealed that the flowers of musa species treat many illnesses like alleviate menorrhagia, dysentery, diabetes mellitus (Singh
heart pain, diarrhea, stomach cramps, infantile malnutrition (Leonard 2006), anaemia and malaria.

Recently, little work has been done on phytochemistry of musa species. Previous studies done have been focused on parts of the plants for instance banana pulps and peels. Phytochemicals in banana plants that have been reported include saponin, saponin glycosides (Salau et al 2010) alkaloids and indole alkaloids (Lewis et al 1999, Pascual-Villalobos 2007), flavonoids and terpenoids (Knapp et al 1969). The bioactive compounds are also used in soap, dyeing and pharma industry.

Banana peel is a rich source of starch (3%), crude protein (6-9%), crude fat (3.8-11%), total dietary fibre (43.2-49.7%), and polyunsaturated fatty acids, particularly linoleic acid and α-linolenic acid, pectin, essential aminoacids (leucine, valine, phenylalanine and threonine), and micronutrients K, P, Ca, Mg (Emaga et al 2007). Except for lysine, content of all essential amino acids are higher than FAO standard. Peels can also be utilized for extraction of banana oil (amyl acetate) that can be used for food flavouring (Archibald 1949). Banana peels are also good source of lignin (6-12%), pectin 10-21%, cellulose (7.6–9.6%), hemicellulose (6.4–9.4%) and galactouronine acid. Pectin extracted from banana peel also contain glucose, galactose, arabinose, rhamnose, and xylose (Emaga et al 2008). Micronutrients (Fe and Zn) were found in higher concentration in peels compared to pulps (Davey 2009). Banana peel can be used in wine, ethanol production and as base material for pectin extraction. Peel ash can be used as fertilizer for banana plants and as source of alkali for soap production (Udosen and Enang 2000). Ethanol extract of *M. sapientum* peels can be used as an inhibitor for mild steel corrosion (Eddy 2008). Peel can also be used in wastewater treatment plants (Memon et al 2008).
Peel is often considered as waste and is used as livestock feeds. Studies show that banana peel contains beta sitosterol, stigma sterol, campesterol, cycloeucalenol, cycloaratanol and 24-methylene cycloartanol, the major constituents are 24-methylene cycloartanol palmitate and unidentified triterpene ketone. Dried banana peel contains 30-40% tannin and used to blacken leather. Ash from dried peel is rich in potash and used for making soap and dyeing.

The nutritional compositional analysis of Yelakkibale, Pachabale and Nendranbale done by Shymala et al (2011) indicated the presence of protein, calcium, iron, polyphenols, tannic acid, ether extractive, ash, dietary fibre, essential amino acid, polyunsaturated fatty acids and potassium. The yield of peel obtained as % of whole fruit was more in Nendranbale with 33%. Water absorption capacity was high for all the three varieties. This was due to high fibre content of peels which consist of a large number of hydrophilic groups that absorb water. Protein content was lowest and tannins was highest and total carotenes was almost negligible in Nendranbale. Total flavonoids were high in both the solvent and aqueous extract of Nendranbale peel. Among all three varieties, Nendranbale peel exhibited high antioxidant activity which could be correlated positively with polyphenols, flavanoids and tannins.

Previous research on preliminary phytochemical screening of dried leaves and fruit peels of Musa paradisiaca revealed the presence of some glycosides, anthrocyanine, tannins, flavanoids and carbohydrate (Alisi et al 2008). No research has been reported on the phytochemical screening of banana flowers except a quantitative study on saponin and flavanoid by Sheng et al (2010) and later phenolic content by Loganayaki et al (2010). The bract part of Musa paradisiaca was reported to contain anthocyannins such as delphinidin, pelaragonidin, peonidin and malvidin (Kitdamrongson 2008,
Pazmino-Duran et al 2001). Total phenolic content in bract was reported as the lowest compared to other parts other parts such as rhizome, fruit peel, ovary, petiole, pseudostem and leaves (Pothavorn 2008). Loganayaki et al (2010) reported higher amount of phenolic in banana flower than in its stem and leaf sample.

As natural sources have many useful and important bioactive compounds and many have been discovered using bioactivity directed fractionation and isolation (BDFI). The research of pharmacognosy or isolation of natural products facilitated new development of bioassay methods. It has been found that the bioactive compounds are mostly plant secondary metabolites, which become medicine after processing to pure compounds; and many useful commercial products. Different type of isolation methods have been used to obtain pharmacologically active compounds which includes isolation from plants and other natural sources, combinatorial chemistry, synthetic chemistry, and molecular modelling.

Alkaloids are natural product that contains basic nitrogen atoms. The name of alkaloids derives from the “alkaline” and it was used to describe any nitrogen-containing base. Alkaloids are naturally synthesis by a large numbers of organisms, including animals, plants, bacteria and fungi. Alkaloids are a group of natural products (also called secondary metabolites). Alkaloids can be easily purified from various crude extracts by acid-base extraction.

The terpenoids sometimes called isopenoids, are a class of natural products which are very similar to terpenes, that have been derived from five-carbon isoprene units and can be interchanged in thousands of ways. Most of the terpenoids have multi cyclic structures that differ from one another by their functional groups and basic carbon skeletons. These types of natural
lipids can be found in every class of living things, and therefore considered as the largest group of natural products.

Terpenoids can be thought of as modified terpenes, where terpenes are hydrocarbons resulting from the combination of several isoprene units. The classification of terpenoids can be made according to the number of isoprene units used.

Triterpenes consist of six isoprene units e.g. squalene found in wheat germ, and olives.

Glycosides is a group of natural product where a sugar group is directly bonded through its anomeric carbon to another group by an O-glycosidic bond or an S-glycosidic bond. The sugar group is then known as the glycone and the non-sugar group as the aglycone or genin part of the glycoside. The glycone can consist of a single sugar group (monosaccharide) or several sugar groups (oligosaccharide).

Phenols or Phenolic are hydroxyl group (-OH) containing class of chemical compounds where the (-OH) bonded directly to an aromatic hydrocarbon group. Phenol is considered the simplest class of this group of natural compounds. Other examples are Resveratrol, Polyphenols (flavonoids and tannins), Gallic acid, Eugenols etc.

An analysis of phytochemical screening of Musa acuminata peel, flower and bract are investigated the existence of primary phytochemcials and the quantitative investigation and DPPH free radical scavenging activities of the extract of Musa acuminata flowers are done with the aim of finding out cost effective bio products which could be used as corrosion inhibitor for mild steel.
1.28 SCOPE AND OBJECTIVES

Mild steels are used extensively in chemical as well as other allied industries. These metal structures are often subjected to cleaning, descaling and pickling by acids which are normally accompanied by considerable dissolution of metal as well as acid consumption. Inhibitors are generally used to control metal dissolution. Most corrosion inhibitors are organic compounds containing heteroatom like O, S and/or N atoms in their aromatic or long carbon chain. The synthetic chemicals though are most effective corrosion inhibitive, they are highly toxic, costly and pose threat to the environment and make it necessary to develop environmentally acceptable and less expensive inhibitors. Non toxic inhibitor formulations are obtained from natural products which can replace those compounds that cause environment pollutants. Natural products are good source of eco friendly corrosion inhibitors. Extracts of naturally occurring plant products contain mixture of compounds and are biodegradable in nature and at the same time offer comparable performance and cost.

Environmentally friendly corrosion inhibitors range from rare earth elements to organic compounds and are used as alternative corrosion inhibitors to reduce the harmful effects on humans, animals and environment. Plant extracts offer several advantages over traditional inhibitors such as chromates. Natural products of plants exhibit high surface activity, so the trend of using them has become increasingly important in recent years. Plant extracts are environmental friendly, bio-degradable, non-toxic, easily available and of potentially low cost. About 100 plant materials have been studied as corrosion inhibitors for mild steel, aluminum, zinc, copper and magnesium. Materials from all different parts of the plant viz., leaves, bark, nuts, flowers, fruits, fruit peels, essential oil, pulpy vegetable matter and seeds have been studied as corrosion inhibitors. The nitrogen heterocycles, tannins,
oxygen containing heterocycles like flavones, coumarins and flavonoids are reported to inhibit corrosion. Use of plant extracts offers higher efficiency because corrosion inhibition is fortified through synergism.

Mild steel was chosen due to its wide range of application, low cost and easy availability. Hydrochloric acids, sulphuric acid and phosphoric acid are the most commonly used acids in pickling baths at high temperatures up to 60ºC. These acids are widely used for pickling such as removal of oxide from the metallic parts before coating, to remove unwanted scale such as rust or mill scale formed during manufacture. Inhibitors are used in industrial process to minimize both the metal loss and acid consumption.

The corrosion inhibitive properties of *Musa acuminata* plant parts such as fruit peel, flower and bract were studied on mild steel in 1N hydrochloric acid, sulphuric acid and phosphoric acid media. All the parts of *Musa acuminata* ‘Nendran’ - a monoecious plant of musa species have medicinal properties. Banana is the most nourishing fruit, contains vitamins and minerals. It is a rich source of energy, low in protein and fat contents and provides a balanced diet.

It is the most nutritious herbal flower rich in vitamins, minerals, essential amino acids and an excellent source of antioxidants. The phytochemical components of *Musa acuminata* flower have been studied and it is known to have tannins, flavonoids, saponin, alkaloid and phenols which are responsible for inhibiting corrosion. The natural flavonoids present in the flower extract exhibit antioxidative activity that stop oxidation and hence corrosion. Aqueous extracts of these plants are effective in retarding the dissolution of metal in acid cleaning process. The presence of electron cloud on the aromatic ring and the electronegative nitrogen or oxygen is likely to induce greater adsorption of the compounds on the surface of mild steel which can lead to effective inhibition.
Though, the literature survey indicates voluminous work carried out by researchers all over the world in these fields separately but there is less report on the study of effect of plant extract in three different acid media and their comparative study. Since no corrosion studies have been reported on *Musa acuminata*, the current study aims to find its corrosion inhibition.

The present investigation deals with the extraction of plant part in various acid media and to evaluate their corrosion inhibiting performance on mild steel surface. Both physicochemical and electrochemical corrosion monitoring methods have been used for the evaluation of inhibition efficiency using various techniques and in the temperature range 303 K – 353 K. Surface examination was also carried out to observe the corrosion inhibition performance. The adsorption characteristic of photochemical of *Musa acuminata* ‘Nendran’ plant was studied to assess the mechanism of corrosion inhibition.

The current study is undertaken with a view to evaluate the performance of the plant parts of *Musa acuminata* as ecofriendly corrosion inhibitor for mild steel in acid media.

Reason for choosing plant extracts as corrosion inhibitors:

- Synthetic inhibitors are toxic and costly.
- As *Musa acuminata* fruit peel is a waste product in the banana chips making industries, it is easily available, and potentially of low cost.
- The extract can be prepared by simple procedure.
- It is biodegradable and non toxic.
The aim of the present investigation is to show the role of *Musa acuminata* plant extracts as natural corrosion inhibitor of mild steel in 1N HCl, 1N H$_2$SO$_4$ and 1N H$_3$PO$_4$ (0.05, 0.10, 0.50, 1.0, 1.5 and 2.0% v/v) environments.

Present work is undertaken with the following objectives:

- To collect *Musa acuminata* ‘Nendran’ fruit peel, floret and bract, extract the plant part in the three different acid media and analyze the phytonutrients of the plant extracts.

- To study the efficacy of the acid extract as corrosion inhibitor for the mild steel in 1N hydrochloric, sulphuric acid and phosphoric acid media, using weight loss method. To examine the effect of concentration and immersion period on inhibition efficiency of the inhibitor.

- To evaluate the efficiency of the inhibitor at elevated temperatures and calculate the thermodynamic parameters.

- To study the potentiodynamic polarization of mild steel in the presence and absence of the plant extracts in the three acid media.

- To analyze the surface of the mild steel sample before and after immersion in the corrosive media with and without the inhibitor using scanning electron microscopy.
To compare the efficiency of the inhibitors in 1N HCl, H$_2$SO$_4$ and H$_3$PO$_4$ and propose a suitable mechanism for the adsorption process.

The schematic representation of the present investigation is given below:
Selection & Collection of plant material (Musa acuminata – ped, flower & bract)

Characterization of plant material

Corrosion monitoring techniques

Preparation of plant extract in 1N HCl, H2SO4, & H3PO4

Phytochemical analysis by spectrophotometer (FTIR & UV-Vis)

Quantitative phytochemical analysis

Qualitative phytochemical analysis

Surface analysis SEM, EDX, FTIR

Impedance measurements

Potentiodynamic polarization studies

Weight loss method

Non-electrochemical

Electrochemical

Weight loss method

Preparation of plant extract in 1N HCl, H2SO4, & H3PO4

Phytochemical analysis by spectrophotometer (FTIR & UV-Vis)

Quantitative phytochemical analysis

Qualitative phytochemical analysis