The metals have been a center of attraction for mankind since earlier stages of life. The first most significant metal manufactured by smelting ore technique was bronze, which ended the Stone Age and began the Bronze Age. The metals have fascinated mankind for many centuries, because these materials have shown unsurpassed properties in wars as well as in general applications. Among all the metals, iron is the most utilized material for industrial and engineering applications [Obot et al., 2011]. Iron is the fourth most common element in the earth's crust as well as one of the most important engineering materials used in manufacturing of various products, such as, cars, airplanes, trucks, roads, railways, buildings and bridges because it is strong, safe to handle, and economical. Generally, metals are extracted from their ores (oxide) and reduced in presence of a reducing agent (smelting). Iron is also extracted from their ores (magnetite, hematite, and limonite), and purified through various processes; however, pure iron (pig iron) is not very useful due to its low strength and brittle nature. So, some common elements like nickel, chromium, manganese, vanadium, titanium, and niobium are deliberately added to enhance the functional properties of iron. Similar to other metals, iron and alloys have a natural ability to compensate their thermodynamic instability via an instant reaction with the environment, which cause oxide film formation on metal surface. In case of other metals, such as, nickel and aluminum, oxide film provides enough protection (passivation) to metal in various environments. On the other side, iron oxides are found highly unstable as iron oxide occupies more volume than iron metal, causing significant metal loss. This specific reactivity of metals on exposure to environments is termed as corrosion [Fontana, 1968]. Corrosion of metals and alloys not only destroy materials functionality but also produce a threat for lives of people, and

involves a huge money investment and human efforts. Therefore, it becomes necessary to deal with the losses and hazards arising from corrosion of metals.

1.1 Concept and Definition of Corrosion

A metal is a solid material of highly unstable nature, and usually not found in its free state in the Earth. Metals are often extracted from their ores via mining, and hence contain high energy. For energy balance, an immediate reaction occurs between metals and their working environments, and metal oxide products are formed on the exposed surface. This natural process is defined as corrosion. The most common example of corrosion we see in daily life is rusting of iron. Iron and steel easily combine with oxygen and water of environment to form hydrated iron oxide, having similar chemical property as iron ore.

Corrosion is considered as a complex problem and may affect metals in different modes. Accordingly, it can be defined in many ways: however, corrosion can be broadly described as chemical or electrochemical deterioration of metals and their functional properties via an instant reaction between metals and its environment. The term corrosion can be used for materials (often for metals), such as, wood, concrete, plastics, ceramics, etc., but it is described as degradation instead of corrosion. The word corrode is adopted from a Latin word 'corrodo', which means "gnaw to pieces". Thus, corrosion can be defined as a process which gradually wears away metals, as if by persistent chewing.

1.2 Economic and Social Effects of Corrosion

The effects of corrosion on mankind can be notified in both direct and indirect manners. In our daily lives, we use various products made of metals like automobile parts, tools,

water heaters, furnaces, doors, grill channels, windows, washers, dryers, and steel bars. These products need scheduled maintenance or sometime complete replenishment, which incurs an additional cost to consumers. In spite of above stated manner, corrosion can financially attack on humans in many other ways. A big example of this problem can be given as corrosion of reinforcing steel bars in concrete structures, which may lead to sudden failure of working structures, such as, bridges, buildings, towers, etc., involving huge money for repairing along with a great risk for public safety. Another aspect of corrosion damage can be seen in industries like chemical, electrical, textiles, paper, sugar mill, Tele communication, etc., which exploit numerous machines for manufacturing of various products or providing services. These machines are constructed from metals (especially iron and steel), malfunctioning of which due to corroded machine parts can cause plant shutdown or any temporary problem in smooth working of machines, which will produce a big loss for industries. Apart from economic effect, corrosion has social consequences also. For example, catastrophic failure of the system, such as, boiler and pipes carrying very sensitive fluid or chemicals, can originate fire, explosion, and release of toxic product, health problems due to escaping harmful product from corroded equipment, and other undesirable issues, which are not only sensitive but also uneconomical for people. Thus, it is evident from above stated facts that there is a strong need to control corrosion of metals and alloys.

1.3 Necessity of the Corrosion Protection

It is clear from facts discussed under section 1.2 that corrosion has economic as well as social effect on human's lives. Herein we are giving some more reasons which strongly favor a need of efficient corrosion protection.

1. India is currently spending 2 lakh crores rupees per annum on corrosion protection of metal and alloys, which is huge money for India and other developing countries (as stated by Mr. Baldev Raj, Director, Indira Gandhi Centre for Atomic Research, during world corrosion organization meet in 2011).

2. Not only developing countries but developed countries also are suffering from corrosion attack. Replenishment and repairing of corroded products incur a huge amount of money to them. The world is bearing a cost of 97 lakh crore rupees due to corrosion damage per year, which is about 3 % of world's GDP.

3. The sudden breakdown of Silver Bridge on Ohio River at Point Pleasant cost the loss of 46 peoples and millions of dollars. A main reason behind this incident was found as disintegration of silver metal due to corrosion fatigue.

4. Gasoline explosions in a sewer (Guadalajara district, Analco, 1992) badly damaged 1600 buildings, and caused serious injury to 1500 peoples. One of the main reasons for this explosion was detected as leakage of gasoline from a corroded steel pipe into the main sewer pipe line, which cost 75 million US dollar for pipeline damages and lives of 215 peoples.

5. One of the biggest accident occurred due to corrosion is Bhopal Gas tragedy. It happened on 3 December 1984 at a Union Carbide subsidiary pesticide plant in Bhopal, India. Due to release of toxic gases from this plant, about 2259 peoples died immediately while another 8000 peoples died within 2 weeks from gas related diseases. The disaster took place because water entered a tank containing Methyl Isocyanate through rusty steel pipes, which produced excess Carbon dioxide amongst other products. The resulting

chemical reaction increased the temperature and pressure beyond the designed limit of the material of tank, which opened tank's safety valves to reduce excess pressure. Accordingly, a large amount of poisonous gases was released into the environment, causing immediate death of working peoples as well as serious health related problems to other peoples of Bhopal city.

The above mentioned examples strongly advocate that corrosion of metals and alloys is a serious problem and must be prevented by a strategic approach, which will save money as well as precious lives of peoples.

1.4 Classification of Corrosion

There are several suggested classification standards which describe corrosion types; however, a broad classification of corrosion can be given on the basis of following three factors-

1. *Nature of the Corrosive Medium*: This classification categorizes corrosion according to physical state of the corrosive medium. Wet corrosion deals with corrosion occurring due to a liquid or moisture while Dry corrosion usually needs a high temperature gaseous environment.

2. *Nature of Corrosion Mechanism*: This category gives emphasis on the mechanism of metal interaction with its environment. Accordingly, corrosion reactions can be classified as electrochemical or chemical.

3. *Appearance of the Corroded Metal*: On this basis, corrosion is either uniform or localized. The key characteristic of uniform corrosion is that metal corrodes at same rate over entire surface, but in localized corrosion only small areas are affected.

On the basis of appearance of corroded metal, localized corrosion can be further subcategorized in following forms-

1. *Galvanic Corrosion*: This type of corrosion occurs due to relative reactivity of metals in an electrolyte solution. On immersion in an electrolyte, metals have a natural tendency to become ionized. This behavior differs from metal to metal, and also specific for a metal. Thus, it is clear that dissimilar metals immersed in an electrolyte will have a potential difference between them, which cause corrosion of relatively less noble metal. The corrosion rate will depend on electrolyte conductivity, reactivity of metal and surface area ratio of cathode (less active metal) to anode (more active metal). A good example of galvanic corrosion can be given as traditional tin can. The tin is a more noble metal with respect to steel, hence steel will corrode at faster rate whenever tin coating breaks. Another example is galvanized iron sheet, which have zinc as a sacrificial anode over iron surface. To avoid galvanic corrosion, one should use metals having competitive position in galvanic series. Dissimilar metals must be covered with an insulation coating, to avoid any contact between them.

2. *Crevice Corrosion*: This corrosion usually occurs at the spaces where activity of the working fluid is limited. In such cases, the confined areas works as a cathode while others act as an anode. Consequently, a cell is formed and corrosion proceeds inside the crevices. Crevice corrosion can be frequently noticed in engineering structures, such as,

welded lap joints, riveted joints, gasket seals, pipe fittings, nut and bolts, and stacked sheets. Aggressiveness of crevice corrosion is governed by crevice type, crevice geometry, corrosive environment, and metallurgical factors. For prevention from crevice corrosion, the components must be designed in such a way that the junction points should be kept open as wide as possible. In some cases, for example scaling problems in tanks, simply scheduled cleaning of the tanks can avoid formation of crevices.

3. *Pitting Corrosion*: This aggressive form of localized corrosion badly diminishes metal's functionality as well as creates tiny holes in the metal, which can cause a great deal of damage in a critical situation. The potential difference between pits and rest surface areas is typically responsible for pitting corrosion. Pitting can be initiated by a small surface defect or a local damage of a protective coating. On contrast, the polished and smooth surface show higher resistance against pitting corrosion. Many alloys which have corrosion resistance due to a passive layer over the surface, such as, stainless steel, nickel alloys and aluminum alloys, are the most susceptible material for pitting corrosion. On the other side, the materials which often corroded uniformly are not attacked by pitting corrosion. For example, normal carbon steel suffers by uniform corrosion whereas stainless by pitting corrosion, in seawater. Pitting corrosion can be avoided by proper surface finish or by alloying with the material having good resistance against pitting.

4. *Stress Corrosion Cracking (SCC)*: It belongs to growth of a crack, either already present in metal or created by any means, in a corrosive media. SCC is highly sensitive to chemical environments, meaning that a material suffer by SCC only when exposed in a number of selective chemical environments. These environments are often one of the weakest corrosive media for a given alloy. For instance, mild steel (a ductile metal)

cracks in the presence of alkali and nitrates, some austenitic stainless steels crack in the presence of chlorides. Stress cracking originates from following three factors- a vulnerable material, a selective corrosive environment, and tensile stresses. To prevent metals from SCC, one should try to eliminate any one of the factors stated above.

5. *Intergranular Corrosion* (IGC): IGC is involved where grain boundaries of crystalline materials are more favorable places for corrosion instead of inside grains. In nickel alloys and austenitic stainless steels, chromium is added to increase corrosion resistance of the alloy. Due to heating effect, chromium carbide precipitates at the grain boundaries, creating chromium deficient zones adjacent to the grain boundaries. This process is called sensitization. In a corrosive atmosphere, the sensitized alloys become highly reactive resulting disintegration of materials at grain boundaries. Weld decay of stainless steels is another example of Intergranular corrosion.

6. *Selective Leaching*: This type of corrosion is often found in solid solution alloys, and occurs due to preferential removal of one constituent of the alloy. Dezincification of brass is the most common example of selective leaching. Due to corrosion, zinc is selectively removed from copper zinc alloy (brass), leaving a spongy mass of copper in dezincified region.

7. *Erosion-Corrosion*: Erosion-corrosion includes the combined action of mechanical wear (due to fluid motion) and a corrosive chemical attack. This type of corrosion is extremely harmful to the alloys that show passivity due to formation of a protective film on their surface. In this case, the abrasive action of the corrosive fluid may erode away the protective layer and generate a bare surface available for corrosion. Erosion-corrosion

can be easily observed in piping system at bends, elbows, and especially where the fluid velocity changes suddenly. One of the best possible prevention methods to retard erosion corrosion is to improve the design in such a manner that turbulence and impingement effects can be avoided. In addition, particulates and bubbles should be removed from the solution, which will reduce erosion effect of the solution.

8. *Corrosion Fatigue*: Corrosion fatigue is a mixed behavior shown by metals under cyclic stresses in a corrosive environment. Nearly all engineering structures encounter some form of alternating stress during their service life. This cause mechanical degradation of metals and can be accelerated in a corrosive environment, causing a great damage to metals. The aggressiveness of corrosion fatigue can be well explained by an example of silver bridge failure in 1967 at Point Pleasant, Ohio. This accident cost millions of dollars, and loss of many peoples. Corrosion fatigue can be prevented via reducing fatigue by minimizing vibration and pressure variation, and reducing corrosion by using high strength alloys having good resistance against corrosion fatigue.

Other Forms of Corrosion:

Microbial Corrosion or Microbiologically Influenced Corrosion (MIC):

MIC is a type of corrosion that is promoted by microorganisms. The microbes react with metals and cause the corrosion or affect other corrosion processes occurring on metallic surfaces. The corrosion causing bacteria can be broadly classified under two categories-aerobic and anaerobic. Aerobic bacteria work in presence of oxygen while anaerobic bacteria do not require oxygen for working. Corrosion of stainless steels at welded joints is a good example of MIC. Basically, damage caused by a bacterial microbe is governed by four other environmental factors: metals (host material), nutrients, oxygen, and water.
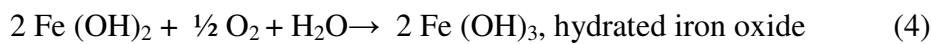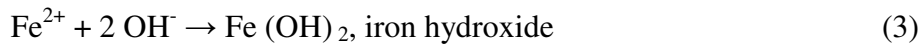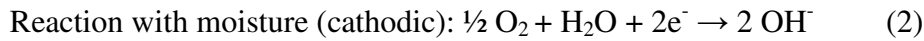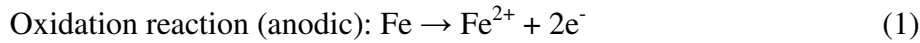
The growth of bacteria requires all four environmental conditions; absence of any one will make these microbes inactive. But, replenishment of environmental conditions will resume the growth of bacteria. Microbial corrosion will only take place at definite temperature ranges and pH of the working media.

Pipeline Corrosion: Pipelines buried in the ground, submerged in water and exposed to the environment, are highly susceptible to corrosion. These unprotected pipelines will eventually corrode lacking proper maintenance. Due to corrosion, structural strength of pipelines can be deteriorated, which makes it risky for transportation of potentially hazardous materials. For prevention of pipeline corrosion, coating and linings are basic tools and usually applied in conjunction with cathodic protection systems.

1.5 Electrochemical Aspects of Corrosion

Corrosion is chemical or electrochemical deterioration of materials as a result of its interaction with the environment. Nearly all corrosion reactions are electrochemical in nature. A complete corrosion reaction comprise of two half reactions, oxidation and reduction. Metals are high energy materials, and release electrons on interaction with the working environment (oxidation). These electrons are consumed by active species (reduction), which complete a corrosion reaction. So, it is evident that for a continuous corrosion process both the reactions should occur simultaneously. The most common example of corrosion is rusting of iron. Iron oxidizes in the moist environment and release electrons for energy balance. Oxygen and water get reduced using these electrons and produce hydroxyl ions. The hydroxyl ions make iron hydroxide via a chemical reaction with iron ions. As the corrosion reaction proceeds, hydrated iron oxide (red)

formed as a final product. The chemical reactions for rusting process are described below-

Oxidation reaction (anodic): $Fe \rightarrow Fe^{2+} + 2e^-$ (1)

Reaction with moisture (cathodic): $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2\ OH^-$ (2)

$Fe^{2+} + 2\ OH^- \rightarrow Fe\ (OH)_2$, iron hydroxide   (3)

$2\ Fe\ (OH)_2 + \frac{1}{2} O_2 + H_2O \rightarrow 2\ Fe\ (OH)_3$, hydrated iron oxide   (4)

Other reduction reactions are also possible, which depend on reducible component of the working environment. A few examples are given below:

$2H^+ + 2e^- \rightarrow H_2$ (5)

$M^{n+} + ne^- \rightarrow M$, M is a metal of n valence   (6)

$O_2 + 2H_2O + 4e^- \rightarrow 4\ OH^-$ (7)

For some metals, such as, aluminium, copper, and stainless steel, oxidation form a protective layer on the surface, this is called as passivity.

On immersion in corrosive solutions or electrolytes, various zones are formed on metal surface. These zones differ in potential due to crystalline imperfections, different phases, and impurities of metals. The potential difference between these areas creates several electrochemical cells (combination of anodic and cathodic regions), through which corrosion of metals proceeds. The developed electrode potential (E) can be well defined by the Nernst equation [Ranney, 1976]:

$$E = E_0 + \frac{RT}{zF} \ln \frac{(ox)}{(red)} \qquad\qquad (8)$$

Where E_0 is standard electrode potential, R is a gas constant (1.98 cal/gm equivalent), F is Faraday constant, T is absolute temperature of reaction, z is number of electrons transferred in reaction, (ox) is the activity of oxidized species (mol/L), and (red) is used for the activity of reduced species. Activity (a) of any element directly vary with the concentration of a moiety (a=γC), where γ is activity coefficient and C is the concentration of a particular element.

1.6 Methods of Corrosion Protection

For corrosion protection of metals and alloys from aggressive attack of corrosion, scientists have used several methods. However, the methods can be fundamentally divided in five categories:

1. *Materials Selection*: Each metal and alloy posses some inherent corrosion resistance. Consequentially, the ability of a material to sustain a corrosion attack differs from metal to metal. For example, gold and platinum are considered as noble metals for their high corrosion resistance, while sodium and magnesium are known as highly active materials and show low resistance against corrosion. Thus, it is evident that a particular metal can affect a corrosion process to a great extent. In addition, the working environment can significantly influence performance of a material. A metal can easily sustain in a particular chemical environment whereas the metal can experience a heavy loss in relatively aggressive environment. So, it can be concluded that the corrosion rate varies directly with corrosivity of environment and inversely with the selected metal. Taking this point into consideration, one can design a safe model for a corrosive media.

2. *Coatings*: The main aim of coatings is to prevent underlying material from corrosion attack. On the basis of type of materials used, coatings can be divided into two broad categories- metallic and nonmetallic.

Metallic Coatings include covering of target materials with a metal's layer. This metallic layer either protects underlying metal or scarifies itself for protection. An example of former application is tin-plated steel, where tin protect steel component. For later one, a good example can be given as galvanized steel, where zinc is preferentially corroded for prevention of steel.

Organic coatings work on isolation of target materials from the working environment. An organic film on metals surface creates a barrier for corrosive media, which limit corrosion attack and protect materials. There are many existing formulation of organic coatings, covering a wide range of service condition for a given product.

Similar to organic coatings, inorganic coatings do the same job, i.e., form a barrier layer for corrosive molecules. Inorganic coatings typically include porcelain enamels, glass coatings and linings, and other corrosion resistant ceramic materials. Some ceramic coatings are also used in wear and heat resistant applications. For example, carbides and silicides are used as a wear resistant and heat resistant material, respectively.

3. *Cathodic Protection*: This method of corrosion protection works on electrochemical theory of corrosion. According to this, an anodic material corrodes faster than a cathodic material. If a metal is forced to remain cathodic, corrosion prevention will occur. There are two methods to provide cathodic protection to a material- impressed current type, in

which target structure is connected to negative terminal of a power source, and sacrificial anode method, which use an anode of active metals, such as, zinc and magnesium.

4. Design: The effective use of rational design principles can avoid many corrosion problems as well as significantly reduce cost and time invested in corrosion control activities. The efficient use of design can eliminate dead spaces or crevices where corrosive media become more aggressive. In case of possibility of stress corrosion cracking failure, the components can be designed taking safety factor in to account, which will ensure safe functioning of that component. Interchangeability and standardization of parts can reduce the losses due to corrosion damage. These practices of rational design principles can be very helpful for management of corrosion losses.

5. *Inhibitors*: A corrosion inhibitor decreases corrosion rate of a material, typically a metal and an alloy. These chemical compounds function via formation of a protective layer on material's surface, which inhibit access of corrosive substances to metal's surface. Some common example of corrosion inhibitors are chromates, silicates, and organic amines. These inhibitors are preferred to use in closed spaces, so that concentration of an inhibitor can be easily maintained. The corrosion inhibitors can affect anodic or cathodic or sometime both reactions. For example, volatile amines are used in boilers to retard the effects of acid. In some cases, amines create an insulating layer on steel surface as well as act as an anodic inhibitor. Corrosion inhibitors are also used in paints formulations. In case of a defect in the coating, inhibitors are released from the coating, and thus corrosion is controlled.

1.7 Definition and Working Principle of Inhibitors

A corrosion inhibitor belongs to a class of chemical compounds that retard corrosion of a material, usually a metal or an alloy, when added in the corrosive environments [Fawcett et al., 1992]. NACE defines a corrosion inhibitor as "A substance which retards corrosion when added to an environment in small concentrations". Another definition given by ISO is "Chemical substance which decreases the corrosion rate when present in the corrosion system at a suitable concentration, without significantly changing the concentration of any other corrosive agent". On a whole, it can be said that inhibitors are chemical compounds that retard corrosion rate of metals and alloys in the corrosive media.

Inhibitors usually adsorb on metals surface and isolate it from the working environment, which cause corrosion prevention. Inhibitors influence corrosion process by either influencing polarization behavior, or retarding movement of ions towards metallic surface, or increasing electrical resistance at the metal-solution interface. However, a more systematic description of working mechanism of inhibitors can be given on the basis of three theories of inhibition.

Adsorption Theory: This theory states that inhibitors slow corrosion process by getting adsorbed on the metallic surface. Adsorption of inhibitor generates an isolative layer on metals, and hence inhibition occurs. An inhibitor can be adsorbed on a surface via either physical or chemical adsorption. In the case of physisorption, inhibitor molecules attract towards metal surface and form a physical bond through electrostatic interaction. On the contrast, chemisorption involves electrons sharing between lone pair or π electrons of inhibitor and metal surface, and thus a coordinate bond is formed.

Hydrogen over Potential Theory: Hydrogen evaluation is one of the most commonly occurring cathodic processes in corrosion reactions. It is a well established fact that most of the inhibitors are of cathodic nature, meaning that they mainly suppress cathodic reactions. These inhibitors retard hydrogen evaluation at cathode, which diminish anodic reactions, and hence corrosion inhibition acknowledges.

Quantum Chemical Theory: This theory suggests that electrons of outer most orbital of an organic compound are directly responsible for chemical bonding with the metal surface. According to this theory, chemisorption is a linear combination of wave functions of participating inhibitor molecules and surface metal atoms. For a chemical bonding, energy of HOMO (Highest Occupied Molecular Orbital) of inhibitor should be greater than energy of LUMO (Lowest Unoccupied Molecular Orbital) of the metal atom. It has been experimentally found that inhibition efficiency directly depends on HOMO. More high energy of HOMO, the more will be inhibition efficiency of an inhibitor.

1.8 Classification of Inhibitors

Inhibitors react with metals and form either a chemical bond or physical bond with the surface atoms, which retards further corrosion of metals. A key factor in selection of an inhibitor is metal and its working environment. So, on that basis, inhibitors can be mainly classified into environmental conditioners and interface inhibitors. However, a broad classification is illustrated in Figure.

1. *Environmental Conditioners (Scavengers)*: As the name suggest, the inhibitors that decrease corrosivity of the medium by scavenging the aggressive substances are called environmental conditioners. In neutral solutions like water, oxygen reduction is one of

the most common cathodic reactions. In this case, corrosivity of the solution can be restricted by decreasing the oxygen content using hydrazine (a scavenger).

2. *Interface Inhibitors*: This type of inhibitors has a general working mechanism for diminishing corrosion attack, i.e., to form a film at metal/solution interface. However, interface inhibitors can be classified into liquid and vapor phase inhibitors.

2.1 *Liquid Phase Inhibitors:* Depending upon the working method, liquid phase inhibitors can be subcategorized into anodic, cathodic, and mixed inhibitors.

2.1.1 *Anodic Inhibitors:* Anodic inhibitors mainly retard the reactions that are occurring at the anodic sites. They form, promote the formation of, insulating films that retard metal corroding reactions. Anodic inhibitors are especially used in near neutral solutions. They are also called passivators. It is worth to mention here that sufficient concentration of anodic inhibitors in a solution is must, otherwise corrosion reactions may be accelerated rather than inhibited. The minimum concentration, of anodic inhibitors, above which they work efficiently, depends on the nature and concentration of corrosive ions. Chromates, nitrates, molybdates are some examples of anodic inhibitors.

2.1.2 *Cathodic Inhibitors*: Cathodic inhibitors stifle corrosion by either inhibiting cathodic reactions or adsorbing selectively on cathodic sites. They are also called as poisons or precipitators. In near neutral or alkaline solutions, inorganic ions, such as, phosphates, and borates, form isolating films that retard corrosion by restricting oxygen diffusion to the metal surface. Cathodic precipitators adsorb on cathodic sites and form insoluble compounds on the metal surface, consequentially corrosion inhibition occurs.

The most frequently used cathodic precipitators are the carbonates of magnesium and calcium.

2.1.3 *Mixed Inhibitors*: Mixed inhibitors show combined action of cathodic and anodic inhibitors, i.e., they affect both anodic and cathodic corrosion reactions. The efficacy of mixed inhibitors belongs to the degree of their adsorption and covering ability of them. Mixed corrosion inhibitors can adsorb on the metal surface via three possible mechanisms: physical adsorption, chemical adsorption, and a combination of both type (film formation).

Physical adsorption occurs due to electrostatic interactions between metal and inhibitor molecules. There are two cases in physical adsorption- first; the metal surface is negatively charged, positively charged organic moieties (inhibitors) directly coupled with metal due to attraction forces, and second; the metal surface carries positive charges, firstly anions, such as halides, adsorb on metal surface and then organic cations adsorb synergistically on the surface.

Chemisorption involves charge transferring or sharing between metal and inhibitor molecules. A chemical adsorption process takes more time than a physical adsorption; however, it is more stable than physical adsorption. As the temperature increases, chemisorption increases and causes greater inhibition.

Adsorbed inhibitor molecules, either by physical or by chemical means, may undergo further chemical reactions, producing polymeric films over the metal surface. The protection ability significantly enhances as the films grow from two-dimensional layers

to three dimensional films up to an order of several hundred angstrom. However, inhibition through these films is effective only if the films are adherent and insoluble.

2.2 *Vapor Phase Inhibitors*: Vapor phase inhibitors or volatile corrosion inhibitors are used for temporary protection against atmospheric corrosion. They have low vapor pressure and can be transported by soaking them in a wrapping paper or by placing them inside a closed container. The slow vaporization of the inhibitor provides protection against air and moisture. In closed spaces like shipping containers, salts of cyclohexylamine and hexamethylene-amine are used to serve inhibition purpose. On contact with metal, the vapor of these salts condenses on the surface and release protective ions if come in contact with moisture.

1.9 Green Corrosion Inhibitors

Scientists and researchers have used many chemical compounds for corrosion inhibition of metal and alloys. A big issue related to the frequent consumption of these chemical inhibitors is their toxicity and high operating cost. Due to environmental concerns, peoples are now turning towards the inhibitors that are natural or at least contain 60% BOD. The biodegradation or biological oxygen demand (BOD) is a measure of how long the inhibitor will persist in the environment. Toxicity of the inhibitors is measured as LC_{50} or EC_{50}. LC_{50} (or LD_{50}) is the concentration of any moiety, in this case inhibitor, required to eat 50% of the total population of the test species. EC_{50} belongs to the effective concentration of an inhibitor (or organic moiety) to adversely affect 50 % of the total population.

Natural products, such as, plants and fruits, contain high content of organic molecules. These molecules can be extracted in some suitable solvents, which are further used for corrosion inhibition. Using natural organic products as a corrosion inhibitor has many advantages over application of synthetic corrosion inhibitors. These inhibitors are biodegradable, non toxic, rich in organic moieties, cost effective, and contain high green value. For an effective inhibitor, general considerations are cost effectiveness and presence of aromatic compounds along with heteroatoms, such as, sulphur, oxygen, nitrogen, incorporated in long chain systems [Singh et al., 1995; Bentiss et al., 2000]. In this regard, the extracts of natural products meet the criteria very well, which have surprisingly increased consumption of them as green corrosion inhibitors.

1.10 Testing of Inhibitors

Inhibitor's performance is rated on the basis of their inhibition efficiency and corrosion rate. For the determination of the same, following methods are used-

1.*Weight Loss Measurements*: A metal or an alloy reacts with the corrosive environments and losses their weights, which depends on the aggressiveness of solution, material's own strength, temperature of the experiment, and pH of an electrolyte. So, inhibition efficiency can be directly related to ability of a corrosion inhibitor to retard metal dissolution in corrosive media. It is one of the easiest and the most accurate methods for evaluation of an inhibitor. For this test, a standard sample is prepared in accordance with ASTM norms and immersed in a solution (at least 5 mL of electrolyte for one cm^2 of metal). The metal is exposed for a certain period of time, and inhibition efficiency is accordingly calculated by the ratio of weight loss in presence of inhibitor to weight loss

in blank solution. The mathematical expressions for determination of inhibition efficiency (μ_{wl}) and corrosion rate (C_r) are given below [El-Etre, 1998]-

$$\mu_{wl}\ (\%) = \frac{W_0 - W_i}{W_o} \times 100 \tag{9}$$

$$C_r\ (\text{mmpy}) = \frac{87.6\ W}{Atd} \tag{10}$$

Where W_0 and W_i is weight loss in absence and presence of inhibitor respectively, W is weight loss in mg, A is surface area of metal immersed in solution, t is time of immersion, and d is density (gm cm^{-3}) of the metal used.

2. *Electrochemical Impedance Spectroscopy (EIS)*: Corrosion of a metal includes transfer of charges (anions and cations) across the metal-solution interface. Accordingly, anticorrosion potential of a corrosion inhibitor is measured from their ability to suppress the charge transferring reactions. Adsorption of inhibitors on metal change charge transfer resistances at the interface, which can be effectively monitored through impedance spectroscopy. EIS records the response of corroding electrodes on application of small-amplitude alternating potential signals of widely varying frequency. This electrochemical method provides accurate information about corrosion reactions, happening at metal-electrolyte interface, via change in impedance and capacitance values. The charge transfer resistances can be calculated from fitting of EIS results, and accordingly inhibition efficiency is computed using following equation [Bentis et al., 2000]-

$$\mu_{Rt}(\%) = \frac{R_t^i - R_t^0}{R_t^i} \tag{11}$$

Where, R_t^i and R_t^0 are the charge transfer resistances without and with inhibitor respectively.
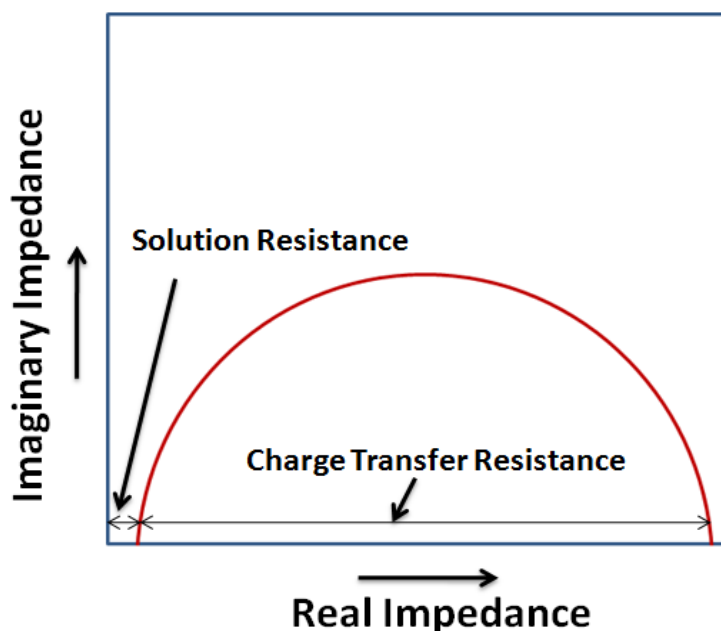

Figure 1.1 Showing various terms of electrochemical impedance spectroscopy

3. *Potentiodynamic Tafel Polarization Test*: Tafel polarization test is a useful tool to predict corrosion mechanism, corrosion rate, and inhibition theory (anodic, or cathodic, or mixed). It is a potentiodynamic method of polarization, i.e., varying voltage is applied to the electrode, by which corrosion cycle of a material can be envisaged through corresponding corrosion current and equilibrium corrosion potential (E_{corr}). Free corrosion potential or E_{corr} can be defined as the potential developed by a metal electrode, in open circuit condition, when it is immersed in an electrolyte. The E_{corr} refers to the point where rate of anodic and cathodic reactions are in equilibrium, i.e., no corrosion will take place. If we deliberately shift potential from equilibrium voltage, either in positive or negative direction, rate of anodic and cathodic reactions will be influenced, indicating effect of an inhibitor on metal corrosion. Tafel polarization test includes application of an over potential voltage η ($V_{applied}$- E_{corr}) to the electrode with reference to

standard electrode. The corresponding curves are extrapolated (as shown in Figure), and corrosion current density (I_{corr}) values are obtained. Inhibition efficiency can be calculated from I_{corr} values by using following equation [Bentis et al., 2000]-

$$\mu_p(\%) = \frac{I^0{}_{corr} - I^i{}_{corr}}{I^0{}_{corr}} \tag{12}$$

Where, $I^0{}_{corr}$ and $I^i{}_{corr}$ belong to corrosion current density values in absence and presence of inhibitor.
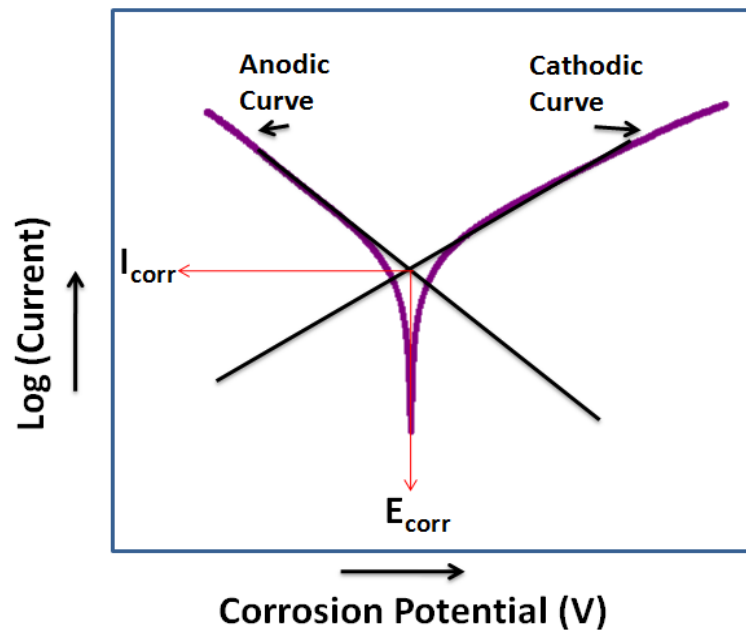
Figure 1.2 Showing various terms of Tafel Polarization curves

4. *Linear Polarization Resistance Test:* Linear polarization resistance (PR) can be defined as the slope of potential-current density curves at equilibrium corrosion potential. Mathematically, it can be calculated by following equation [Lagrenee et al., 2001]-

$$I_{corr} = \frac{b_a * b_c}{2.303\ (b_a + b_c) * PR} \tag{13}$$

23

Accordingly, Inhibition efficiency μ_{PR} can be determined using following equation [Lagrenee et al., 2001]-

$$\mu_{PR}(\%) = \frac{PR^i - PR^o}{PR^i} \qquad (14)$$

Where, b_a and b_c are the slopes of anodic and cathodic polarization curves, and PR^i and PR^0 are the linear polarization resistance values in presence and absence of inhibitor respectively.

5. *Adsorption Isotherm Fitting*: Generally, inhibitors adsorb on the metal surface and form a protective film at the metal-solution interface, and hence corrosion retards. Thus, it is evident that inhibition efficiency of a corrosion inhibitor is a function of its adsorption on a metal or an alloy. To access the details of adsorption process, various isotherms are used, such as, Langmuir, Frumkin, Temkin, Freundlich, Flory-Huggins, and El-awady; however, exact adsorption mechanism can be known after fitting of surface coverage (θ) values as a function of inhibitor concentration (C). Some of them are described below-

The Langmuir isotherm establishes a relation between the molecular adsorption of a moiety on a solid surface and concentration of a medium. The Langmuir equation can be written as-

$$K_{ads}C = \frac{\theta}{1 - \theta} \qquad (15)$$

Where, K_{ads} is the equilibrium constant of adsorption process.

The Langmuir equation is based on some basic assumptions: if a surface has n vacant sites, the probability of adsorption on each site will be equal and every site will adopt only one molecule. This isotherm model is valid for both type of adsorption, i.e., chemical and physical.

Temkin and Frumkin isotherm models can be presented by following equations-

$$K_{ads}C = e^{f\theta} \quad \text{(Temkin)} \tag{16}$$

$$K_{ads}C = \frac{\theta}{1-\theta}e^{f\theta} \quad \text{(Frumkin)} \tag{17}$$

Where, $f\theta$ is used for the configuration factor that varies with the physical model and assumptions considered during derivation of the equation.

6. *Thermo Gravimetric Tests*: Corrosion rate of a metal varies with various active parameters. Among all, temperature is the most important factor as corrosion rate exponentially increases with temperature rise. Hence, it becomes necessary to test thermal stability of a corrosion inhibitor. Relation of corrosion rate and temperature can be described very well by Arrhenius equation [Martinez and Stern, 2002]-

$$\ln C_r = \ln A - \frac{E_a}{RT} \tag{18}$$

Where, C_r belongs the corrosion rate, Ea is the apparent activation energy of corrosion process, R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is absolute temperature (Kelvin), and A is the Arrhenius pre-exponential factor. Other kinetic parameters, such as, change in enthalpy (ΔH^*) of activation, and entropy (ΔS^*) of activation, can be computed from Transition state equation [Martinez and Stern, 2002]-

$$\ln \frac{C_r}{T} = \left(\ln \frac{R}{Nh} + \frac{\Delta S^*}{R} \right) - \frac{\Delta H^*}{RT} \tag{19}$$

Where N denotes Avogadro's number (6.022×10^{23} molecule mol^{-1}) and h is the Planck's constant (6.626×10^{-34} J sec mol^{-1}).

Another important parameter related to corrosion is change in Gibbs free energy (ΔG) that can be defined as a chemical potential of a reaction. If it is positive: no reaction will take place, if it is negative: reaction will proceed, if it is zero: that will indicate equilibrium between forward and reverse reactions. Gibbs free energy of a reaction can be correlated to K_{ads} via following equation [Mu et al., 2004]-

$$\Delta G^0 = -RT (\ln K_{ads}) = -2.303\ RT (\log_{10} K_{ads}) = -nFE^0 \tag{20}$$

The standard adsorption free energy can also be related to equilibrium adsorption coefficient K_{ads} by following given equation [Mu et al., 2004]-

$$K = \frac{1}{C_{solvent}} \exp(\frac{-\Delta G^0}{RT}) \tag{21}$$

Where, $C_{solvent}$ is the concentration of water in solution (1×106 mg L^{-1}).

1.11 Importance of Mild Steel Protection

Mild steel (MS) is an alloy of iron containing carbon not more than 0.25%. MS shows excellent mechanical properties, such as, ductility and malleability, and posses a fair tensile strength. In several industrial and engineering applications, MS is frequently used for its cheap cost and high machinability [Ellayyachy et al., 2006]. Several industries, like paper, sugar, textile, petrochemical, and food, employ machines for manufacturing of the products. These machines, or some of their parts, are made of mild steel. During maintenance process, mineral acids, especially HCl and H_2SO_4, are used for cleaning.

The acids not only remove dust particles, oil, grease, and oxide layer over the machine parts but also aggressively corrode MS. Consequentially the continuous corrosion of MS parts can catastrophically choke manufacturing process, which will incur a great loss to the industries.

1.12 Literature Survey on Corrosion Inhibitors

Before use of inhibitors, to mitigate corrosion of metals, peoples were centered towards the application of metallic and organic coatings. Their use was definitely effective, but this method of protection included much time, hard labor, and high cost. Hence, a necessity of an effective method, that could minimize the efforts and cost of protection, was come up, which originated corrosion inhibitors.

Inhibitors work on mixed potential theory. This theory (Wagner) states that (a) an electrochemical reaction include two or more partial oxidation and reduction reactions [Wagner and Traud, 1938], (b) the electrical charges will be conserved during an electrochemical reaction, i.e., no net accumulation of charge, and (c) the electrical potential at the whole surface of an isolated metal electrode will be equal in magnitude.

In starting age of inhibitors, several chemical compounds were used for inhibition study; however, problems like high synthesis cost and complicacy of synthesis procedure, and toxicity motivated scientists to work in a new direction of green and cheap inhibition. In this regard, the natural products, like plants, waste biomass and fruit peels, have shown excellent anticorrosion potential for corrosion inhibition of metals and alloys. We have illustrated their working method through literature survey that is sequentially described below.

A.Y. EL-Etre [1998] investigated anticorrosion potential of natural honey for corrosion inhibition of copper in a 0.5 M sodium chloride solution. A good inhibition efficiency of 97.6 % (1000 ppm) was reported; however, the inhibition efficiency decreased with time due to the growth of fungi in the medium. The adsorption of natural honey on the copper: chloride interface was found to follow the Langmuir isotherm.

The inhibitive effect of 2,5-disubstituted-1,3,4-oxadiazoles on the corrosion of mild steel in 1 M HCl and 0.5 M H_2SO_4 had been studied by *F. Bentiss et al.* [2000]. It was reported that these compounds were very good inhibitors and retarded corrosion mainly by diminishing the cathodic reaction. The adsorption of oxadiazole derivatives on mild steel in both acidic media were found in accordance with Langmuir isotherm model.

M. Lagrenee et al. [2001] reported substituted oxadiazoles as corrosion inhibitors for mild steel in acidic medium. Above 90% inhibition efficiency was achieved using these chemical compounds. One interesting fact of this report was that one of the studied molecules (PAOX) inhibited corrosion of mild steel, while another molecule (PNOX) accelerated corrosion rate of mild steel.

The corrosion inhibition efficiency of a triazole derivative, namely 3,5-bis (4-methylthiophenyl)-4H-1,2,4-triazole had been investigated in 1 M HCl and 0.5 M sulfuric acid by *M. Lagrenee et al*. [2002]. Nearly 90% corrosion inhibition was acknowledged in 1 M HCl, while it was 80% in 0.5 M sulfuric acid. Adsorption of this organic molecule on metal surface was found in accordance with Langmuir adsorption isotherm.

H.L. Wang et al. [2002] synthesized a mercapto-triazole compound, namely 4-salicylideneamino-3-phenyl-5-mercapto-1,2,4-triazole (SAPMT), and investigated its anti corrosion potential for mild steel in 1.0 M hydrochloric acid (HCl) solution. It was

analyzed from the obtained results that the SAPMT molecule that includes phenyl, mercapto and azomethine groups in the same molecule had higher protection efficiency than the corresponding compounds which did not contain the above mentioned functional groups.

A.Y. EL-Etre [2003] found that Opuntia extract acted as a good corrosion inhibitor for aluminum in 2.0 M HCl. Through investigation, it was revealed that the inhibition efficiency (IE) increased with the increase in inhibitor concentration. A maximum inhibition of 96% was acknowledged using the extract. In case of adsorption mechanism, Langmuir isotherm was found as the suitable candidate.

The anticorrosive property of Zenthoxylum alatum plant extract in aqueous orthophosphoric acid had been studied by G. *Gunasekaran et al.* [2004]. An excellent inhibition efficiency of 98% was obtained using the extract. Monitoring of the metal-inhibitor interaction by XPS and FT-IR showed that the protective layer of inhibitor compounds present in plant extract, iron oxide and iron phosphate. In addition, it was found that formation of inhibiting iron phosphate was catalyzed by the formation of Fe–PE organo metallic complex.

F. Bentiss et al. [2004] had synthesized 2,5-Bis(4-dimethylaminophenyl)-1,3,4-oxadiazole (DAPO) and 2,5-bis(4-dimethylaminophenyl)-1,3,4-thiadiazole (DAPT), and studied their inhibitive effect on mild steel corrosion in 1M HCl and 0.5 M H_2SO_4. It was found that DAPT performed better than DAPO in both acid media. Langmuir adsorption isotherm showed the best fitting for both molecules. It is worth to mention here that DAPO and DAPT are considered as non-cytotoxic substances.

A.Y. EL-Etre et al. [2005] tested the aqueous extract of the leaves of henna (lawsonia) for corrosion inhibition of C steel, nickel and zinc in acidic, neutral and alkaline solutions, and reported on the basis of obtained results that the extract performed as a good corrosion inhibitor for the three test electrodes in all tested solutions. The Inhibition efficiency of the extract followed the order: For C-steel and nickel, alkaline < neutral< acid; while in the case of zinc, acid < alkaline < neutral. It was found that the extract functioned as a mixed inhibitor and adsorbed on metal in accordance with Langmuir isotherm in all tested systems.

The adsorption and inhibitive effect of khillah (*Ammi visnaga*) seeds on the dissolution of SX 316 steel in HCl solution was reported by *A.Y. EL-Etre* [2006]. The inhibition efficiency was found to be increased with the inhibitor concentration. The formation of insoluble complexes, as a result of interaction between iron cations and khellin (present in the extract), was reported responsible for anticorrosion potential of the extract.

J.E. Pereira da Silva et al. [2007] did an interesting work on active corrosion protection of metals using different conducting blends, formed by doped polyaniline (PANI) and poly (methylmethacrylate) (PMMA). They investigated the influence of two different dopants, camphorsulfonic (HCSA) and phenylphosphonic acids (HPPA), of PANI on the anticorrosion performance for different metals. In all the metal/blend systems, a potential shift to more positive values than the potential of uncoated metals in acid solution was noticed, which indicated inhibited metal substrate.

P.B. Raja et al. [2008] evaluated the effect of the extract of black pepper on mild steel in 1M H_2SO_4 solutions and found that the black pepper extract acted as a good corrosion inhibitor, even at high temperatures also. The adsorption process was reported

responsible for inhibition, which was in accordance with Temkin isotherm. From the study, it was concluded that the extract retarded both anodic and cathodic reactions, i.e., mixed type inhibition.

Some plant extracts, leaves extract of Occimum viridis (OV), Telferia occidentalis (TO), Azadirachta indica (AI) and Hibiscus sabdariffa (HS) as well as seed extract of Garcinia kola (GK), were studied for their anticorrosion potential for mild steel in 2 M HCl and 1 M H_2SO_4. *E.E. Oguzie* [2008] found that the inhibition efficiency increased in following order: TO>AI>HS>GK>OV. Also, the effect of halide additives on inhibition efficiency was investigated.

P.C. okafor et al. [2008] reported the leaves, seeds, and a combination of leaves and seeds extracts of *Phyllanthus amarus* for mild steel corrosion in HCl and H_2SO_4 solutions . The maximum corrosion inhibition was obtained using leaf extracts. The adsorption properties of the inhibitors were described by Temkin isotherm model.

S.K. Shukla et al. [2008] synthesized functionalized self doped conducting polymer (polyanthrilic acid) and tested as a corrosion inhibitor for mild steel in acidic environment. This water soluble polymer (100 mg L^{-1}) provided more than 90% corrosion inhibition in 0.5 M HCl.

The adsorption properties of the extracts of leaves and seed of *Gossypium hirsutum L.* in 2 M NaOH solutions were studied by *A.K. Abiola* et al. [2009]. They reported that the leave extract (97% efficiency) was more effective than the seed extract (94%).

S.K. Shukla et al. [2009] synthesized 4-substituted anilinomethylpropionate namely 3-anilinomethylpropionate (I-1), 3-(4-methylanilino) methylpropionate (I-2) and 3-(4-chloroanilino) methylpropionate (I-3) and tested them as corrosion inhibitors of mild

steel in 1 M HCl solutions. It was found that I-3 was the most efficient inhibitor among studied compounds, followed by I-2 and I-1. All the inhibitors were found to work in a mixed mode of inhibition.

The effect of Aloe vera leaf extract on zinc corrosion was investigated by *O.K. Abiola* et al. [2010] in 2 M HCl. A maximum inhibition efficiency of 67% was achieved using 10% v/v concentration of the extract. It was found that inhibition efficiency increased with the extract concentration but decreased with the temperature rise. The adsorption of the inhibitor molecules on zinc surface was in accordance with Langmuir adsorption isotherm.

S.A. Umoren et al. [2010] investigated Pachylobus edulis exudate gum for corrosion inhibition of mild steel in 2 M H_2SO_4. In addition, the effect of potassium halide additives on inhibition efficiency of inhibitor was also studied. It was reported that halide additives synergistically increased the efficiency of the exudate gum. The adsorption properties of the inhibitor were studied in the temperature range of 30-60˚ C, and it was found at all studied temperature that molecular adsorption of inhibitor molecules over metal surface followed Temkin isotherm.

U.F. Ekanem et al. [2010] tested pineapple leaves extract for retarding mild steel corrosion in HCl solution. Additionally, the effect of temperature on inhibitor's performance was studied in the range of 30-60˚ C. The extract successfully retarded corrosion of steel and adsorbed on metal surface according to Langmuir isotherm model. The chemical adsorption of inhibitor on metal was suggested as the corrosion inhibition mechanism on the basis of obtained kinetic and thermodynamic parameters.

The effect of alkaloids of *Isertia coccinea* plant on the corrosion of C38 steel 1 M HCl was studied by *M. Lebrini* et al. [2011]. A maximum inhibition efficiency of 91% was achieved using the plant extract. The *Isertia coccinea* plant extract was found working in a mixed inhibition mode. Various isotherms, Langmuir, Temkin and Frumkin, were tested to clarify the nature of adsorption; however, the best fitting was obtained for Langmuir isotherm model.

The Karanj (Pongamia pinnata) seed extract was exploited by *A. Singh* et al. [2011] for corrosion inhibition of mild steel in hydrochloric acid solution. Along with the determination of inhibition efficiency of the seed extract, the effects of temperature, immersion time, and acid concentration on the corrosion behavior of mild steel were also studied. The extract showed excellent potential against acid induced corrosion (98% efficiency) by diminishing both cathodic and anodic partial reactions. The adsorption of inhibitor molecules was confirmed by FTIR spectroscopy, which was in accordance with Langmuir adsorption isotherm.

I.B. Obot et al. [2011] synthesized a phenanthroline derivative, 2-mesityl-1H-imidazo[4,5-f][1,10]phenanthroline (MEIP), and tested for its anti corrosion potential for mild steel in 0.5 M H_2SO_4 solution. The maximum corrosion inhibition (87% at 303 K) was acknowledged for 10 µM concentration of the inhibitor. The corrosion inhibition efficiency was determined at various temperatures (303-333 K), which revealed that inhibition efficiency decreased with temperature rise suggesting that inhibitor molecules were physically adsorbed on the metal surface. Also, quantum chemical and statistical methods were used to study the metal-inhibitor interaction.

Caulerpa racemosa (a marine alga) was reported by *C. Kamal* et al. [2012] for its potential against mild steel corrosion in 1 M HCl solution at the temperatures 303, 313, and 323 K. More than 80% corrosion inhibition was obtained using 25 ppm concentration of the extract. The molecular adsorption of the extract on the mild steel surface was found to obey Temkin isotherm model. The AFM images also confirmed adsorbed inhibitor molecules (caulerpin) over metal surface, which retarded acid corrosion of mild steel.

M.A. Chidiebere et al. [2012] investigated corrosion inhibiting effects of Punica granatum on mild steel corrosion in acidic environments. A maximum inhibition efficiency of 84.8 % and 83.2 % was acknowledged in 0.5 M H_2SO_4 and 1 M HCl respectively. The results showed that the organic matters of the extract were adsorbed on metal and retarded both cathodic and anodic corrosion reactions. The adsorption behavior of inhibitor was also discussed by the density functional theory.

S. Deng et al. [2012] studied the inhibition effect of Ginkgo leaves extract on the corrosion of cold rolled steel in 1.0–5.0 M HCl and 0.5–2.5 M H_2SO_4. Nearly 92% and 80% corrosion inhibition was achieved using the extract in 1M HCl and 0.5 M H_2SO_4 solutions. The investigation revealed that adsorption of inhibitor obeyed Langmuir isotherm model, and behaved as a mixed type inhibitor in HCl while as a cathodic inhibitor in H_2SO_4.

X. Li et al. [2012] had reported the bamboo of Dendrocalmus sinicus Chia et J.L. Sun leaf extract for protection of cold rolled steel corrosion in 1.0–5.0 M HCl and 0.5–2.5 M H_2SO_4. The results revealed that the extract performed better in HCl than H_2SO_4. A maximum inhibition efficiency of 90% and 80% was acknowledged in hydrochloric acid

and sulfuric acid solutions. The bamboo extract molecules were found attached with CRS surface and the adsorption of them followed Langmuir adsorption isotherm.

The inhibitive effect of ethanol extract of Acalypha torta leaves (EAL) on mild steel in 1 M HCl solution was studied by [42] *P. M. Krishnegowda* et al. [2013]. Nearly 90% corrosion inhibition was obtained using 100 ppm of the extract. Langmuir adsorption isotherm was found to govern the adsorption of inhibitor molecules on mild steel. Through analysis, it was reported that the extract was a mixed type inhibitor.

E.E. Oguzie et al. [2013] had explored the extracts of the fruit of Capsicum frutescens for anticorrosion and antimicrobial activity. The corrosion studies were performed on the ethanol extract of the fruit. It was reported through investigation of the results that the phytochemcial constituents of the extract, such as alkaloids (8.8%), tannins (0.4%), and saponins (39.2%), adsorbed on the low carbon steel and hence inhibition acknowledged. Molecular dynamics (MD) simulations were also executed to theoretically explain the electronic structure and adsorption behavior of the fruit extract.

S.A. Umoren et al. [2013] exploited date palm (Phoenix dactylifera) seed extracts for corrosion inhibition of mild steel in 1 M HCl and 0.5 M H_2SO_4 media. The maximum inhibition efficiency of 89% and 87% was acknowledged in HCl (2.5 g L^{-1}) and H_2SO_4 (1.5 g L^{-1}), respectively. The effect of immersion time was also studied for the extract. The Langmuir isotherm model had provided the best fitting for the results obtained, indicating validity of the approach taken.

The torsemide and furosemide drugs were investigated for their anticorrosion potential against mild steel dissolution in 1 M HCl by *S.H. Kumar* et al [2013]. Results indicated that torsemide performed better than furosemide in all the experimental studies. The

mechanism of corrosion inhibition was proposed as adsorption of inhibitor molecules on metal surface, which retreaded both cathodic and anodic partial reactions. The adsorption process was in accordance with Langmuir isotherm. The influence of temperature on inhibition efficiency was studied along with determination of quantum chemical parameters.

M. A. Velázquez-González et al. [2014] evaluated performance of Rosmarinus officinalis as a corrosion inhibitor for carbon steel in 0.5 M H_2SO_4 solutions. The organic matter of this herb was extracted in acetone, hexane and methanol solvent, and used further for corrosion inhibition studies. The best result was obtained by using the hexanic extract that adsorbed on the metal surface. The better corrosion resistance of steel in presence of inhibitor could be attributed to flavonoids of the extracts.

M. Bozorg et al. [2014] investigated performance of Myrtus Communis extract as a green corrosion inhibitor for copper in sulfuric acid solutions. Results indicated that Myrtus Communis extract efficiently (89% efficiency, 100 mg L^{-1}) inhibited corrosion of copper. It was reported that the extract behaved as a mixed type inhibitor. The adsorption of the extracts molecules was found to obey Langmuir isotherm model.

1.13 Choice of Inhibitors for the Study

Through vigilant analysis of the literature, we found that the organic moieties that contain heteroatoms, such as S, O, and N, lone pair electrons, and π electrons in their chemical structures were excellent as a corrosion inhibitor. Despite above mentioned technical requirement, another important consideration for selection of inhibitors is their green value. In the last few years, the environmental issues are being addressed very carefully.

The synthetic inhibitors are very efficient, at the same time, they are toxic and costly. Hence, scientists and researchers have been working for many years to develop a corrosion inhibitor that can compete with existing inhibitors and contain high green value. In this regard, we have selected three natural organic products, Argemone Mexicana (Plant leaves), Chlorophytum Borivilianum (root), and Banana (peels). The reasons for selecting them for corrosion inhibition studies are given in details below-

Argemone Mexicana, Papaveraceae family, is a cheap plant and easily available in surroundings. In Indian Ayurvedic therapy, the various parts of this plant have been used since ancient years to cure skin diseases, inflammations, and stomach pain. It is also famous as Svarnakshiri in Ayurvedic system. Argemone Mexicana plant possesses excellent medicinal properties, but the plant also contains alkaloids that make it toxic. However, it is reported that the aqueous extract of the plant leaves do not contain alkaloids and hence do not show toxicity. The leaves of *Argemone Mexicana* contain several biodegradable organic molecules, such as proteins, amino acids, tannins, phenolic compounds, saponins and flavonoids along with non-alkaloids organic compounds like fused benzene rings, hetero N atom rings, $-OCH_3$ and $-OH$ groups [Dash and Murthy, 2011]. These organic moieties of the extract meet with general requirements of a corrosion inhibitor. So, we have selected this plant for corrosion studies.

Chlorophytum Borivilianum, Liliaceae family, is an herb with lanceolate leaves. In India, it is more popular as 'Safed Musli'. Due to high medicinal values, the roots of this herb are more frequently used than other parts of the plant. In Ayurvedic therapeutic system, Safed Musli is used as a nutritional tonic that cures sexual weakness. Consumption of *Chlorophytum Borivilianum* root power also increases the activities of antioxidant

enzymes and vitamin C levels. Additionally, *Chlorophytum Borivilianum* contains high content of saponins, flavonoids, and other effective aromatic organic molecules [Kenjale et al., 2007], which fulfills the general criteria of an effective inhibitor. Hence, we have selected the roots of *Chlorophytum Borivilianum* for our study.

Bananas (*M. Paradisica*) are widely consumed in the world market for their high nutritional values. Due to high vitamin content, many industries, like agro and food processing industries, also consume banana fruits in manufacturing of various products. A main problem associated with the frequent consumption of banana is that people or industries consume only edible part of banana fruit (pulp) and do not use non edible part (peel), conventionally. Thus, banana peels go waste and they are thrown as such in the environment, which can cause serious health problems (after ripening) for humans. It is worth to mention here that banana peel is surprisingly found to contain higher content of micronutrients than banana pulp [Davey et al., 2007]. That is one of the reasons to select banana peels for the study. M. Paradisica, Musaceae family, is a rich source of various bioactive compounds. In India, it is known as bhusawal keli. The bioactive compounds of banana peel, such as, gallocatechin, catechin, ascorbate, and dopamine [Someya et al., 2002] as well as low cost (almost free), easy availability, and high green value (recycling of a waste material) make the peel attractive for consideration. So, we have selected banana (*M. Paradisica)* peel for corrosion inhibition studies.

1.14 Motivation and Objectives of the Work

Through literature survey, I have found that natural products have been widely tested as corrosion inhibitors. Peoples have reported that extraction of natural organic molecules

from natural products is easier than synthesis of chemicals. Also, these molecules are equally efficient as chemical inhibitor. The cost effectiveness and high inhibition efficiency motivated me to do my research work in this area. However, there are some weak points in current working trends in this field, which must be effectively addressed to ensure the effective utilization of natural products. The points are as follows-

1. Uneconomical and unbalanced use of Natural Products.

2. High Inhibitor concentration for corrosion prevention.

3. Unemployment of waste natural products as corrosion inhibitors.

4. Random selection of natural products without proper justification.

5. There are only few reports that include effects of change in various parameters, such as, acid concentration, temperature and immersion time, in one work.

In the view of above crucial points, the following objectives are considered for my present work-

1. To screen the cheaper natural/waste natural products for corrosion inhibition study on the basis of presence of aromatic rings and hetero-cyclic groups.

2. To investigate anticorrosion potential of *Argemone Mexicana*, *Chlorophytum Borivilianum* and *M. Paradisica* for corrosion inhibition of mild steel in HCl and H_2SO_4 solutions.

3. To study the effect of change in various parameters, viz., temperature, acid concentration and immersion time, on the inhibition efficiency of inhibitors.

4. To analyze mild steel-inhibitor interaction by FTIR spectroscopy, UV-Visible spectroscopy, adsorption isotherms, SEM, and AFM.

5. To find out the reasons of inhibitive performance of the selected inhibitors and propose a suitable corrosion inhibition mechanism.