Chapter I
Introduction
1. GENERAL INTRODUCTION

1.1 Definition of Corrosion and its Importance

Corrosion can be defined in many ways. Some definitions are very narrow and deal with a specific form of corrosion, while others are quite broad and cover many forms of deterioration. The word corrosion refers to the degradation of a metal by its environment. The simplest definition of corrosion refers corrosion as the deterioration of a material or its properties by chemical or electrochemical reaction when interacting with its surrounding environment. The technical definition of corrosion given by International Standard Organization (ISO) worked out in collaboration with International Union of Pure and Applied Chemistry (IUPAC) defined corrosion as the “Physicochemical interaction between a metal and its environment which results in changes in the properties of the metal and which may often lead to impairment of the function of the metal, the environment or the technical system of which these forms a part” [1, 2]. However, the above definition did not include non metallic materials, which are also corroded when exposed to their environments. Therefore, an alternative definition of corrosion was suggested which refers corrosion as “an irreversible interfacial reaction of a material (metal, ceramic, and polymer) with its environment which results in consumption of the material or in dissolution into the material of a component of the environment” [3]. Corrosion is a natural process of deterioration and most metals corrode on contact with water, acids, bases, oil and salts. The main reason for metals to corrode is their tendency to return to their naturally occurring forms which is accompanied by a decrease in the free energy of the system.
The importance of corrosion was recognized in the sixties when it was realized that damage was being caused to the economics of the industrialized nation, resources are being wasted by anti-metallurgical process and useful life of manufactured goods were being reduced [4]. The corrosion, an inherently difficult phenomenon to understand, is a widely researched subject as it involved issues pertaining to the human life and safety, huge environmental and economic impact, and conservation of materials. The effects of corrosion in our daily lives are both direct, in that corrosion affects the useful service lives of our possessions, and indirect, in that producers and suppliers of goods and services incur corrosion costs, which they pass on to consumers. The environmental impact and economic losses are the prime motive for much of the current researches in the field of corrosion. The economic losses due to corrosion are divided into direct losses and indirect losses [5]. Direct losses are those losses associated with the direct replacement of corroded industrial equipment, machinery or their components such as pipelines, condenser tubes, and replacement of various parts of equipments and plants. Perhaps most dangerous of all is corrosion that occurs in major industrial plants, such as electrical power plants or chemical processing plants. Plant shutdowns can and do occur as a result of corrosion. Indirect losses are more difficult to assess and contains plant shutdown, loss of efficiency, loss of products as well as contamination of products and over design.

1.2 Cost of Corrosion

Corrosion has a major impact on the economy of a nation. The economic losses due to corrosion to the worldwide industry are staggering. It is estimated that 25% of the total product of the metal and alloys go waste due to corrosion. In every
country each year industries are paying huge price for corrosion and that cost is rising. It is estimated that the annual cost of corrosion in the United States is in the range of $9 billion to $90 billion. These figures were confirmed by various technical organizations, including the National Association of Corrosion Engineers. The first comprehensive landmark study on losses due to corrosion was carried out in USA in late seventies. The results of study showed that the total loss due to corrosion in the year 1975 was $70 billion which was approximately 5% of Gross National Product (GNP) of that year [6]. Another study conducted in the US estimated the annual direct cost of corrosion to be staggering at $276 billion which is approximately 3.1% of the nation’s GDP [7]. A report on the cost of corrosion in India estimated the annual losses due to corrosion to be Rs 25,000 crores per year which works out to be 4% of GNP [8]. Approximately one third of the cost of corrosion is avoidable and could be saved by using corrosion resistant materials and application of state-of-the-art corrosion control technologies. A number of other studies on the economic losses due to corrosion carried out at various times and in various industrialized nations suggest that corrosion consumes 3-5% of GNP of that particular nations.

1.3 Corrosion Measurement Units

The corrosion rate may be expressed as an increase in corrosion depth per unit of time (penetration rate, for example, mils/yr) or weight loss per unit area per unit time, usually mdd (milligrams per square decimetre per day) or the corrosion current (mA/cm²). Though preferred SI unit of corrosion rate expression is mm/yr or inch/yr, the expression mils per year (mpy) (a mil being a thousand of inches) is the most widely used and desirable corrosion rate expression in USA.


![Equation Image]

where, \( W \) is weight loss in mg; \( \rho \) is the density of specimen in g/cm\(^3\); \( A \) is the area of specimen in sq. in. and \( t \) is exposure time in hrs.

### 1.4 Electrochemical Theory of Corrosion

The electrochemical theory is the only theory which is universally accepted and is applicable to most of the corrosion processes. Corrosion in an aqueous or an atmospheric environment involves an electrochemical process which involves the transfer of electrons between a metal surface and an aqueous electrolyte solution. An electrochemical process consists of an anode, a cathode, an electrolyte for ionic conduction and electron path for electron conduction. A corrosion reaction, in general, is the sum of two complementary electrode processes; an anodic process involving the oxidation of the metallic material, making electrons available in the metallic phase and a cathodic process which consumes the electron made available by the anodic process, through a reduction reaction.

**Anodic process:** The anodic reaction in every corrosion reaction is the oxidation of a metal to its ion which passes into solution:

\[
M \rightleftharpoons M^{n+} + ne^{-} \tag{1.2}
\]

where, \( n \) is the valence of metal, \( e^- \) indicates the electron, \( M \) generic metallic material and \( M^{n+} \) its ion which passes in to the solution. In cases where the metallic material tends to form hydroxides, the anodic reactions are of following type:

\[
M + nH_2O \rightleftharpoons M(OH)_n + nH^+ + ne^- \tag{1.3}
\]
Cathodic processes: The cathodic processes involve reduction reaction and are indicated by the consumption of electrons. In aqueous solution various reduction reactions are possible depending upon the environment, which occurs at the cathode. The possible reduction reactions are as follows:

\[ 2H^+ + 2e^- \rightarrow H_2 \text{(gas)} \]  
\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]  
\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]  
\[ 2H_2O + 2e^- \rightarrow H_2 \text{(gas)} + 2OH^- \]  
\[ M^{3+} + e^- \rightarrow M^{2+} \]  
\[ M^{2+} + 2e^- \rightarrow M \]

During corrosion process, more than one oxidation and one reduction reaction may occur and the anodic and cathodic reactions occurring during corrosion are mutually dependent.

1.5 Corrosion Prevention and Control Methods

Corrosion control is the application of engineering principles and procedures to minimize corrosion to an acceptable level by the most economical method. The various methods of corrosion control are as follows:

1.5.1 Materials selection

The selection of the proper metal or alloy for a particular corrosive service is a common method of preventing corrosion. It is of major importance in the chemical process industries. A criterion for selection of ferrous and non-ferrous materials in
equipment of construction is largely dependent on stability for the intended service, availability, ease of fabrication and cost- economics. Carbon and low alloy steels are the most widely used materials of construction as they satisfy all the above criteria i.e., they are easy to fabricate, easily available and are inexpensive [9]. The physical and chemical properties of the oxide film formed on an alloy and the service environment determine the corrosion resistance of the alloy. Stainless Steels are extensively used in petrochemical plants because of the highly corrosive nature of the catalysts and solvents that are often used [10]. The corrosion resistance of stainless steels is due to the protective nature of the surface oxide film that forms a barrier between the environment and the alloy. High silicon cast irons (with 14% Si) are extremely corrosion resistant because of a passive surface layer of silicon oxide that forms during exposure to many chemical environments [11]. Tantalum is resistant to most acids at all concentrations and temperatures and is generally used under conditions where minimal corrosion is required, such as implants in the human body. High-nickel cast iron (with 13 to 36% Ni and up to 6% Cr) has excellent corrosion, wear and high temperature résistance because of the relatively high alloy content [12]. Copper and copper-nickel alloys are widely used in marine application. Titanium is also susceptible to crevice corrosion in hot seawater and other hot aqueous chloride environments.

The choice of a corrosion resistant material is quite complicated and is accomplished in several stages. There are also metallurgical factors, such as crystallography, grain size and shape, grain heterogeneity, second phases, impurity inclusions, and residual stress that can influence corrosion. Thus, alloying,
metallurgical treatments, and mechanical treatments can greatly affect the corrosion resistance of the resulting alloy.

1.5.2 Proper design

Corrosion control makes the greatest economic sense at the design phase. The proper choice of materials and pro-active detailing can provide handsome savings of maintenance dollars, at very little cost expense. The mistakes in plant design are the most frequently cited cause (58%) of corrosion failure in chemical process industries. Proper design for corrosion control must include consideration of proper material selection, finish selection, drainage, sealants, galvanic coupling of materials, application of corrosion-inhibiting compounds, access for maintenance, the use of effective corrosion control programs in service, and consideration of environmental issues. Designs that introduce local stress concentrations directly or as a consequence of fabrication should be carefully considered.

1.5.3 Protective coatings

The application of protective coating is one of the popular options of corrosion control [13]. Essentially, protective coatings are a means for separating the surfaces that are susceptible to corrosion from the factors in the environment which cause corrosion to occur. They give long terms protection under a broad range of corrosive conditions, extending from atmospheric exposure to full immersion in strongly corrosive solution. The application of a surface coating is common with a number of different products, ranging from electrical wiring to printed labels. The coatings are also helpful in preventing rust or enhancing the function of the product, as in the case
of coated cookware. One of the most common examples of protective coatings is electrical wiring. The wires that actually carry the flow of current are covered with polymer coatings designed to contain power generated by the wires. At the same time, the coating protects the wires from exposure to any outside element that could cause a short or corrode the wires. The protective coatings in themselves provide little or no structural strength, yet they protect the materials so that the strength and integrity of a structure can be maintained. The protective coatings are further classified into following types:

1.5.3.1 Organic coatings

These coatings afford protection by providing a physical barrier between the metal and the environment. It is most widely used protective coating and is being used for protecting aluminium, zinc and carbon steel against corrosion. According to the Department of Commerce Census Bureau, the total amount of organic coating material sold in the United States in 1997 was 5.56 billion L, at a value of $16.56 billion. The total sales can be broken down into architectural coatings, original equipment manufacturers (OEM) coatings, special-purpose coatings, and miscellaneous paint products. These coatings can also contain corrosion inhibitors. Organic coatings include paints, resins, lacquers, and varnishes. Heavy organic coatings, such as mastics and coal tars, are sometimes used to protect aluminum surfaces that are embedded in soils and concrete.
1.5.3.2 Inorganic coatings

These coatings are also used to provide a barrier between the environment and the metal. Inorganic coatings also include enamels, glass linings, and conversion coatings. The treatments change the immediate surface layer of metal into a film of metallic oxide or compound which has better corrosion resistance than the natural oxide film and provides an effective base or key for supplementary protection such as paints.

1.5.3.3 Metallic coatings

Metallic coatings are another type of coating which provide a barrier between the metal substrate and the environment. In addition, metallic coatings can sometimes provide cathodic protection when the coating is compromised. Metallic coatings and other inorganic coatings are produced using a variety of techniques, including hot dipping, electroplating, cladding, thermal spraying, and chemical vapor deposition.

1.5.4 Changing the environment

Environment also provides a versatile means for reducing corrosion. For aqueous corrosion, the environment can be made less aggressive by removing constituents or modifying conditions that facilitate corrosion. This can be achieved by decreasing temperature, decreasing velocity, preventing access of water and moisture, removing dissolve oxygen, and increasing pH for steel. However, this method is limited to closed system in which changes in the corrosion medium can be tolerated.
1.5.5 Cathodic protection

Cathodic protection can be applied in practice to protect metals, such as steel, copper, lead, and brass, against corrosion in soils and in almost all aqueous media. When an external electric current is applied to a metallic structure to be protected, the corrosion rate can be reduced to practically zero. Under cathodic protection, the metal can remain indefinitely in a corrosive environment without deterioration. Cathodic protection was first suggested by Sir Humphrey Davy in 1824 that copper could be successfully protected against corrosion by coupling it to iron or zinc [14]. The most rapid development of cathodic protection was made in the United States of America and by 1945, the method was well established to meet the requirements of the rapidly expanding oil and natural gas industry, which wanted to benefit from the advantages of using thin-walled steel pipes for underground transmission. It is often most cost effective course of action for the corrosion protection. The method is now well established and is used on a wide variety of immersed and buried facilities and infrastructure, as well as reinforced concrete structures, to provide corrosion control. Cathodic protection can be used effectively to minimize corrosion fatigue, intergranular corrosion, stress corrosion cracking, dezincification of brass, or pitting of stainless steels in seawater, or steel in soil. It can however be fairly expensive in the consumption of electric power or the extra metals involved in controlling the potential within this region. Cathodic protection is also applied to canal gates, condensers, submarines, water tanks, marine piling, offshore oil-drilling structures, chemical equipments, bridge decks, parking garages, and other reinforced concrete structures. Cathodic protection is fundamental to preserving a pipeline's integrity. Cathodic protection is a method of corrosion control that is achieved by supplying an
external direct current that neutralizes the natural corrosion current arising on the pipeline at coating defects. Current required to protect a pipeline is dependent on the environment and the number and size of the coating defects. For a particular environment, greater the number and size of coating defects, the greater the amount of current required for protection. Coating plays an integral part in the functioning of a pipeline's cathodic protection system. The principle involved in cathodic protection is to change the electrode potential of the metallic structure so that it lies in the immunity region as shown in Figure 1.1. Within this region the metal is in the stable form of the element and therefore corrosion reactions are impossible. In electrochemical terms, there are two types of cathodic protection applying to a metal structure:

1.5.5.1 Impressed current method

Impressed current cathodic protection (ICCP) technique is widely used for the protection of buried pipelines and the hulls of ships immersed in seawater. A d.c. electrical circuit is used to apply an electric current to the metallic structure. The negative terminal of the current source is connected to the metal requiring protection. The positive terminal is connected to an auxiliary anode immersed in the same medium to complete the circuit. The electric current charges the structure with excess electrons and hence changes the electrode potential in the negative direction until the immunity region is reached. The layout for a typical impressed current cathodic protection system is shown in Figure 1.2. ICCP is most specialized technology and can be very effective if correctly designed and operated. Typical materials used for anodes are graphite, silicon, titanium, and niobium plated with platinum. Coatings are
often used in conjunction with ICCP systems to minimize the effect of corrosion on marine structures. One of the difficulties in designing a combined coating and ICCP system is that coatings deteriorate with time. Precious metals are used for impressed-current anodes because they are highly efficient electrodes and can handle much higher currents. Precious metal anodes are platinized titanium or tantalum anodes; the platinum is either clad to or electroplated on the substrate. Impressed current systems are more complex than sacrificial anode systems and mostly used to protect pipelines.

1.5.5.2 Sacrificial anode method

The principle of this technique is to use a more reactive metal in contact with steel structure to drive the potential in the negative direction until it reaches the immunity region. Figure 1.3 illustrates the principle, in which sacrificial metals used for cathodic protection consist of magnesium-base and aluminum-base alloys and, to a lesser extent, zinc. No external power source is needed with this type of protection system and much less maintenance is required. These metals are alloyed to improve the long-term performance and dissolution characteristics. Sacrificial anodes serve essentially as sources of portable electrical energy. For cathodic protection of offshore platforms, aluminum anodes, made from aluminum-zinc alloys, are the preferred material [15]. Most offshore petroleum-production platforms use sacrificial anodes because of their simplicity and reliability, even though the capital costs would be lower with impressed-current systems. Magnesium anodes have been used offshore in recent years to polarize the structures to a protected potential faster than zinc or aluminum alloy anodes. Magnesium tends to corrode quite readily in salt water, and most designers avoid the use of magnesium for permanent long-term marine cathodic
protection applications. Zinc anodes are also used to protect ballast tanks, heat exchangers, and many mechanical components on ships, coastal power plants, and similar structures. In seawater, passivity can be avoided by alloying additions, such as tin, indium, antimony, or mercury. The three most common types of sacrificial anodes are: activated aluminum, zinc and magnesium. Aluminum is the most widely-used material for anodes, as it has a higher current capacity in comparison to the other metals. Magnesium should be considered when the chloride content is less than 10,000 ppm.

1.5.6 Anodic protection

Anodic protection is an electrochemical method of controlling corrosion and is based on the phenomenon of passivity. Passivity refers to the loss of chemical reactivity experienced by certain metals and alloys under particular environmental conditions. This method is most often used in highly corrosive environment to protect metal immersed in solution with uncommonly acidic or basic qualities. Anodic protection can be used to control the corrosion of metals in chemical environments that exhibit very interesting behavior when subjected to anodic polarization. To anodically protect a structure a device called potentiostat is required. When the potential of the working electrode relative to the reference electrode is controlled and shifted in the more positive direction, the current required to cause that shift varies. If the current required for the shift has the general behavior with respect to potential, shown in Figure 1.4, the metal is termed active passive and can be anodically protected. If the metal was in passive state its corrosion rate could be reduced. Anodic protection is applicable only to metals and alloys which are readily passivated when
anodically polarized and for which \( i \) passive is very low. Anodic protection has been used for storage vessels, process reactors, heat exchangers, and transportation vessels. The primary advantages of anodic protection are its applicability in extremely corrosive environments and its low current requirements. It is not applicable, for example, to zinc, magnesium, cadmium, silver, copper, or copper-base alloys.

### 1.5.7 Use of corrosion inhibitors

The application of corrosion inhibitors is another prevalent method used for corrosion control in closed systems. Corrosion inhibitor may be defined as a chemical substances which, when added in small concentration to an environment effectively reduces the corrosion rate of a metal exposed to that environment [16]. Corrosion processes, being surface reactions, can be controlled by inhibitors which adsorb on the reacting metal surface. The term adsorption refers to molecules attached directly to the surface, normally only one molecular layer thick, and not penetrating into the bulk of the metal itself. In general, an inhibitor forms a protective film in situ by reaction with the corroding surface and as a result, the rate of the anodic and cathodic reactions are retarded. Corrosion inhibition is reversible and a minimum concentration of the inhibiting compound is required to maintain the inhibiting surface film. The effectiveness of corrosion inhibitors is dependent on the metal to be protected as well as on the operating environment. They reduce the corrosion rate by:

- Increasing or decreasing the anodic and/or cathodic reaction
- Decreasing the diffusion rate for reactants to the surface of the metal
- Decreasing the electrical resistance of the metal surface
Inhibitors are mostly used in three types of environments:

- Re-circulating cooling water systems (e.g., of internal combustion engines, rectifiers, and cooling towers) in the range of pH 5 to 9.
- Primary and secondary production of crude oil and subsequent process and
- Pickling acid solution for the removal of dust and mill scale during the production and fabrication of metals parts or post service cleaning.

The inhibitors can be classified into the following types:

1.5.7.1 Passivating (anodic) inhibitors

This type of inhibitors (e.g., chromates and phosphates) acts by preventing the anodic reaction. The inhibitors are incorporated into the oxide film on the metal, thereby stabilizing it and preventing further dissolution. They cause the anodic curve of polarization to shift such that less current flows. They have the ability to passivate the metal surface. The passivating-type inhibitors are very efficient and reduce corrosion rates to very low values. Some alkaline compounds such as NaOH, Na₃PO₄, and Na₂B₄O are known to facilitate passivation of iron byfavoring adsorption of dissolved oxygen. There are two categories of passivating inhibitors namely, oxidizing anions and non-oxidizing anions. Oxidizing anions have the ability to passivate metal in the absence of oxygen. Typical oxidizing anions are chromate, nitrite and nitrate. Non-oxidizing ones such as phosphate, tungstate and molybdate require oxygen to perform passivation. However, one major drawback of such inhibitors is that in order to maintain sufficient passivation of the metal and thus
providing sufficient inhibition, the concentration of the inhibitor must be kept well above a critical or minimum concentration. If the concentration is below the minimum value, it is likely that the metal, which is to be protected in the first place, will suffer from localized corrosion such as pitting. Phosphate is widely used as an additive in boiler water or cooling circuits and in pickling baths for metals. These inhibitors slow down anodic reaction by forming passive film on the metal surface in presence of oxygen.

1.5.7.2 Precipitation inhibitors

This class of inhibitor (e.g., zinc salts) block the cathodic reaction by precipitating at the cathode due to elevated pH values locally. They precipitate on the metal surface, forming a protective barrier. Hard water is rich in magnesium and calcium. When these salts precipitate on the metal surface, for example at the cathode where the pH is higher, they establish a protection layer on the metal.

1.5.7.3 Cathodic inhibitors

Those substances, which reduce the cathodic area by acting on the cathodic sites and polarize the cathodic reactions, are called cathodic inhibitors [17]. Cathodic inhibitors reduce the rate of cathodic reaction namely, oxygen reduction in near neutral environments and hydrogen evolution in acid solutions, respectively.

1.5.7.4 Organic inhibitors

The inhibitors used for protection of steel in acidic solution are generally organic inhibitor. These types of inhibitors are film-forming in nature. They form a
hydrophobic layer on the surface of the metal to prevent dissolution of metal. Most organic inhibitors are substance, which possess at least one functional group considered as the reaction center for the adsorption process. The adsorption of the inhibitor is related to the presence of heteroatom such as nitrogen, oxygen, phosphorus and sulfur as well as triple bond or an aromatic ring in their molecular structure through which they can adsorb on the metal surface [18-21]. The efficiency of this type of inhibitors depends upon the chemical composition and molecular structure of the compounds as well as their affinity with the metal. They are further classified into organic anodic and cathodic or both depending on the reaction mechanism and the potential of the metal at the interface [22].

1.5.7.5 Inorganic inhibitors

The common inorganic inhibitors used are crystalline salts, for instance, sodium chromate and molybdate. The addition of heavy metal ions like Pb\(^{2+}\), Mn\(^{2+}\), Cd\(^{2+}\) is found to inhibit corrosion on iron in acidic medium. This may be due to the deposition of these metal ions over the iron surface [23].

1.5.7.6 Mixed inhibitors

Corrosion inhibitors are rarely used as a single compound. The formulation can be composed of two or more inhibitors which will carry different characters. The use of mixed inhibitors is due to following three main factors:

- A single inhibitor can only inhibit a few numbers of metals. When the environments involve multi-metal system, the inhibitive action may sometimes cause jeopardizing effects to other metals.
• Advantages from anodic and cathodic inhibitors can be combined and optimized for best performance.

• Addition of halide ions improves the action of organic inhibitor in acid solutions

1.5.7.7 Neutral inhibitors

These inhibitors include cathodic inhibitors, anodic inhibitors and mixed or general inhibitors [24]. The compounds used in neutral media are borates, molybdates and salts of organic acids like benzoates and salicylates.

1.5.7.8 Vapor-phase corrosion inhibitors

Vapor-phase corrosion inhibitors or volatile corrosion inhibitors (VCIs) are similar to organic adsorption-type inhibitors. These inhibitors possess moderately high vapor pressure and consequently can be used to inhibit atmospheric corrosion of metals without applying VCIs directly on the metal surface. Volatile corrosion inhibitors are secondary-electrolyte layer inhibitors that possess appreciable saturated vapor pressure under atmospheric conditions, thus allowing vapor-phase transport of the inhibitive substance” [25]. They are usually effective if used in enclosed spaces such as closed packages or the interior of machinery during shipment [26]. Vapor phase inhibitor function by forming a bond on the metal surface or by forming a barrier layer to aggressive ions.
1.6 Corrosion Protection of Steel in Acid Solutions Using Green Corrosion Inhibitors

1.6.1 Introduction

Though all the known materials are susceptible to corrosion the subject of steel corrosion has received considerable attention during the last few decades [27]. Mineral acids are widely used in various industries for pickling of steel at elevated temperatures up to 60 °C. This technique besides being used to remove corrosion scales from steel surface without causing acid attack of the bulk metal is also effectively applied in cleaning of industrial equipment and acidization of oil well [28]. There are several method of preventing corrosion and the rates at which it can propagate with a view of improving the lifetime of metallic and alloy materials. The use of inhibitors is one of the most effective, practical and economic methods to protect metallic surfaces against corrosion in aggressive acidic media [29-31]. Most of the efficient pickling inhibitors are organic compounds containing hetero atoms such as sulfur, nitrogen, oxygen, phosphorus, and multiple bonds or aromatic rings in their structures [32, 33]. The number of lone pairs of electrons and loosely bound $\pi$-electrons in these functional groups are the key structural features that determine the inhibitive action of these compounds [34, 35]. These compounds prevent corrosion by blocking the active corrosion sites either by getting adsorbed, or by forming a protective layer or an insoluble complex on the metal surface. The effectiveness of an organic inhibitor depends mainly to its chemical structure and physiochemical properties of the compounds like functional groups, aromaticity and/or presence of conjugated bond, nature and number of bonding atoms [36]. In addition to this, other
factors such as molecular size and the nature of the substituent groups and heteroatom 
present in the organic compounds also govern the effectiveness of the compounds as 
corrosion inhibitor [37-42]. Other considerations in selection of an inhibitor are the 
cost of the inhibitor, its availability and environmentally acceptability. However, most 
of the organic compounds used as corrosion inhibitors are toxic and hazardous to both 
human beings and the environment [43] and needs to be replaced by nontoxic, 
environment friendly compounds. As a result, the current research trends is towards 
the development of nontoxic, economical and more environmentally safe green 
chemicals as corrosion inhibitors [44-48]. Naturally occurring substances of both 
plants and animal origin otherwise tagged ‘green inhibitors’ are known to meet these 
requirements. In the past two decade, the research in the field of ‘‘green’’ or “eco-
friendly” corrosion inhibitors has been directed towards the goal of using cheap, 
effective compounds at low or ‘‘zero’’ negative environmental impact [49-53].

1.6.2 Plant extracts as green corrosion inhibitors

In recent years, there is a considerable amount of effort devoted to develop 
biodegradable and efficient green corrosion inhibitors extracted from natural plants. 
Plant extracts, in addition to being environmentally friendly and ecologically 
acceptable, are inexpensive, readily available and renewable. The extracts of *Azariecta 
indica*, *Fenugreek* leaves, *Zenthoxylum alatum*, *Opuntia*, *Nypa fruticans*, *Ocimum 
viridis*, *Phyllanthus amarus*, *Chamomile*, *Halfabar*, and *Murraya koenigii* were 
studied as corrosion inhibitors in sulphuric and/or hydrochloric acid medium [54-60]. 
Chauhan and Gunasekaran [61, 62] studied the corrosion inhibition of steel by eco-
friendly *Zenthoxylum alatum* plant extract in HCl as well as in phosphoric acid
medium. Other plant extract like opuntia [63], lawsonia [64] and khillah [65] have been evaluated for corrosion inhibition of metals like Cu, Al, Zn and steel. Other than the plant extracts, pure organic compounds extracted from natural products such as ascorbic acid [66], succinic acid [67], caffeine [68], Pennyroyal oil [69], and caffeic acid [70] have also been used for inhibition of corrosion. Eddy and Ebenso [71] studied the adsorption and inhibitive properties of ethanol extract of Musa sapientum peels as green corrosion inhibitor for mild steel in H₂SO₄ using hydrogen evolution and thermometric methods. The different concentration of ethanol extract of M. sapientum peels was found to inhibit mild steel corrosion. In a very recent paper the corrosion inhibition by extract of Stevia rebaudiana leaves on mild steel in sulphuric acid solution was reported [72]. The techniques used are electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. The inhibition, which was assumed to occur via adsorption of the inhibitor molecules on the metal surface, was found to increase with increasing concentration of the leaves extract. The adsorption of the extract on the mild steel surface obeys the Langmuir adsorption isotherm. Ouariachi et al [73] investigated the inhibition effect of Rosamarinus officinalis oil as green corrosion inhibitor on C38 steel in 0.5 M H₂SO₄. Quraishi et al [74] reported the corrosion inhibition properties of black pepper extract in mild steel in HCl solution by weight loss, potentiodynamic polarization, and EIS. It was shown that black pepper extract gave maximum inhibition efficiency of 98% at 120 ppm at 35 °C. Electrochemical measurements revealed it to be a mixed- type inhibitor. Noor [75] investigated the temperature effects on the corrosion inhibition behavior of mild steel in 2 M HCl and H₂SO₄ in the absence and presence of aqueous extract of fenugreek leaves (AEFL) by gravimetric method. It was shown that the AEFL
inhibited mild steel corrosion in HCl more than in H₂SO₄ at all inhibitor concentrations and solution temperatures. The inhibition action of AEFL was performed via adsorption of the extract species on mild steel surface. The adsorption was spontaneous and followed Langmuir adsorption isotherm in HCl, while followed Temkin adsorption isotherm in H₂SO₄ at all studied temperatures.

The inhibition performance of plant extract is normally ascribed to the presence of complex organic species including tannins, alkaloids and nitrogen bases, carbohydrates and proteins as well as hydrolysis products in their composition. These organic compounds usually contain polar functions with nitrogen, sulfur, or oxygen atoms as well as triple or conjugated double bonds or aromatic rings in their molecular structures, which are the major adsorption centers.

1.6.3 Polymers as green corrosion inhibitors

The use of polymers as green corrosion inhibitors have drawn considerable attention recently due to their inherent stability and cost effectiveness. Owing to the multiple adsorption sites, polymeric compounds adsorb more strongly on the metal surface compared with their monomer analogues [76] Therefore, it is expected that the polymers will be better corrosion inhibitors. The polymer inhibitors which have been examined include: polyethylene glycol, polyvinyl alcohol, polyvinyl pyridine, polyvinyl pyrrolidone, polyethyleneimine, polyacrylic acid, poly acrylamide and starch [77-82]. Umoren et al [83] studied the corrosion inhibition behavior of mild steel in H₂SO₄ in the presence of naturally occurring polymer gum arabic (GA) and synthetic polymer polyethylene glycol (PEG). It was found that PEG was more effective than GA.
Studies on the use of some macromolecules or natural polymers which are green inhibitors have been carried out. For instance, Eddy et al [84] carried out gas chromatography-mass spectroscopy (GC-MS) study to elucidate the chemical structure of *Anogessus leocarpus* gum (AL) and also investigated its corrosion inhibition potential for mild steel in solutions of HCl. The analysis of AL indicated the presence of sucrose (10.03%), phthalic acid (2.53%), n-hexadecanoic acid (11.73%), oleic acid (30.49%), pentacenequinone (4.41%) and 2,3-diphenylnaphthoquinone (21.43 %). The adsorption of the inhibitor on mild steel surface was found to be exothermic, spontaneous, Langmuir type and supports the mechanism of charged transfer from the inhibitor’s molecule to the charged metal surface. *Guar gum* has been shown to be an effective corrosion inhibitor for some metals in aggressive acid environment [85]. Inhibition efficiency was found to increase with increase in the concentration of the tested material. Umoren et al [48] reported the corrosion behavior of exudate gum from *Raphia hookeri* (RH) gum as a potential eco-friendly inhibitor for mild steel in H2SO4 using weight loss and hydrogen evolution techniques at 30-60 °C. The inhibition efficiency was observed to increase with increase in RH concentration but decreased with rise in temperature, which is suggestive of physical adsorption mechanism. The adsorption of the exudate gum onto the steel surface was found to follow the Langmuir adsorption isotherm.

Corrosion inhibition of mild steel in hydrochloric acid by betanin as a green inhibitor in 1 M HCl solution was studied by weight loss method, potentiodynamic polarization, and electrochemical impedance spectroscopy techniques under the influence of various experimental conditions [86]. The polarization curves showed that betanin behaves mainly as a mixed-type inhibitor. Maximum inhibition efficiency
(98%) is obtained at betanin concentrations of 0.01 M. The results obtained from weight loss, polarization, and impedance measurements are in good agreement. Obot et al [87] studied the effect of Sulphathiazole (STZ) as green corrosion inhibitor at mild steel in 0.5 M HCl at different temperature using gravimetric and quantum chemical techniques. It was shown that STZ acts as inhibitor for steel corrosion even at very low concentration. The adsorption process was found to obey the Temkin adsorption isotherm. The calculated activation and Gibbs free energy values confirm the chemical nature of the adsorption process. It is most probable that the inhibition property of STZ was due to charge sharing between the inhibitor molecules and the metal surface.

1.6.4 Amino acids as green corrosion inhibitors

It has been shown by a number of investigators that some amino acids can act as corrosion inhibitors, which has generated an increasing interest in these compounds [88-102]. Amino acids are attractive as corrosion inhibitors because they are relatively easy to produce with high purities greater than 99% at low cost and are nontoxic, biodegradable and completely soluble in aqueous media. Among the amino acids sulfur containing amino acids has been found to be more efficient corrosion inhibitor [103-109].

El-Nabey et al [103] reported the electrochemical measurements and corrosion behavior of mild steel specimens immersed in 1 N H2SO4 solution in the presence and absence of amino acids at room temperature. Inhibition increased with increasing additive concentration and showed that adsorption of the amino acids on the steel surface occurs in two steps: firstly a monolayer of the adsorbate is formed on the
metal surface, and this is followed by the deposition of a second adsorbate layer. The corrosion inhibition of iron in 1 M HCl using twenty two different common amino acids and four related compounds was investigated using potentiodynamic polarization curves [110]. The best results were obtained with 3, 4-diiodotyrosine, with an inhibition efficiency of 87%. The best common amino acid was tryptophan with an inhibition efficiency of 80%. Hydroxyproline, cystine, and cysteine acted as corrosion accelerators. In general, amino acids with longer hydrocarbon chains showed greater inhibition. Additional groups or groups which increased electron density on alpha amino group also increased the inhibition efficiency. Kalota and Silverman [111] showed the corrosion inhibition of steel by aspartic acid. At pH less than the ionization constant of aspartic acid it accelerated corrosion. Above that pH, it acted as an inhibitor for the steel. Abdel et al [112] studied the corrosion inhibition behavior of eleven amino acids namely, glycine, alanine, serine, phenylalanine, tyrosine, tryptophan, histidine, aspartic acid, cysteine, cystine, and methionine on mild steel corrosion in 3 M H₂SO₄ by electrochemical techniques. Among the studied amino acids sulphur containing amino acids were found better corrosion inhibitors. The inhibition efficiencies of cysteine, alanine, valine, phenyl alanine, serine and threonine on the corrosion of steel in 2 M H₂SO₄ were studied by mass loss and gravimetric technique at 25 °C [113]. It was showed that the inhibition efficiency depends on the type of amino acids and its concentration. The inhibition efficiency varies from 42% to 91%. Nineteen different naturally occurring amino acids including methionine were studied as corrosion inhibitor for mild steel in H₂SO₄ using Tafel polarization curves [104]. The best corrosion inhibition was obtained with the S-containing amino acids. The inhibiting performance of five amino acids, on steel in 1
M H\textsubscript{2}SO\textsubscript{4} solution, using potentiodynamic method was investigated [114]. The maximum efficiency was obtained with glutamic acid.

The corrosion inhibition action of four amino acids containing sulfur namely, cysteine, N-acetylcysteine, methionine and cystine on the corrosion of mild steel in phosphoric acid solution polluted with Cl\textsuperscript{-}, F\textsuperscript{-} and Fe\textsuperscript{3+} ions were studied using potentiodynamic and electrochemical impedance techniques [115]. Cysteine and N-acetylcysteine showed higher inhibition efficiency than methionine and cystine. Both F\textsuperscript{-} and Fe\textsuperscript{3+} ions stimulated mild steel corrosion while Cl\textsuperscript{-} ions inhibited the corrosion. The inhibition effect of three amino acids namely, alanine, glycine and leucine against steel corrosion in 0.1 M HCl solutions was investigated by potentiodynamic polarization method [91]. Corrosion parameters such as corrosion rate, corrosion potentials (E\textsubscript{corr}) and corrosion resistance (R\textsubscript{p}) were determined by extrapolation of the cathodic and anodic Tafel region. Adsorption isotherm was investigated by weight-loss measurement. The effect of inhibitor concentration and acid concentration against inhibitor action was investigated. The inhibition efficiency was found to depend on the type of amino acid and its concentration. The inhibition effect of the amino acids was found to range from 28-91%. The adsorption of amino acid followed Langmuir adsorption isotherm. Moretti et al [116] investigated the inhibition effect of tryptamine as green corrosion inhibitor for iron in 0.5 M deaerated H\textsubscript{2}SO\textsubscript{4} (temperature range 25-55 °C) by means of potentiodynamic curves and electrochemical impedance spectroscopy (EIS). Trypatamine was found to be an effective ARMACO iron inhibitor, even at 55 °C and 72 h, but only at 10 mM. At this concentration the inhibition percentage, calculated by potentiodynamic curves and EIS, ranged from 90% to 99% and did not diminish with increase in time and
temperature. Tryptamine adsorption follow Bockris-Swinkels’ isotherm. The thermodynamic data indicated that in the more concentrated solution, tryptamine also chemisorbed on the iron surface. Abiola [106] showed the adsorption of methionine at mild steel surface from acidic solution studied by using gravimetric technique. The adsorbability of methionine was found to depend on the nature of the acid and concentration of methionine. The surface coverage with the adsorbed methionine was used to calculate the free energy of adsorption, $\Delta G^\text{ads}_0$ using Bockris-Swinkel isotherm. The dependence of $\Delta G^\text{ads}_0$ on surface coverage q is due to heterogeneous nature of the mild steel surface.

Alagbe et al [117] investigated the effect of different amino acid namely, leucine, alanine, methionine and glutamic acid on the corrosion characteristics of NST-44 mild steel in lime fluid (citrus aurantifolia) using weight loss immersion method. The corroded surfaces of the specimens were characterized using optical microscopic technique. Alanine showed the highest inhibitive potential on NST-44 mild steel in the lime fluid at lower concentration while glutamic acid showed the least potential. Leucine and methionine, however, showed considerable potentials with inhibition efficiencies of about 41 and 44.70%, respectively. Olivares et al [118] studied the corrosion inhibition of steel in 1.0 M HCl by decylamides of $\alpha$-amino acids derivatives using gravimetric and electrochemical techniques. Protection efficiencies of 90% were obtained with 100 ppm of tyrosine and glycine derivatives, while alanine and valine derivatives reached only 80%. The order of increasing inhibition efficiency was correlated with the modification of the molecular structure of inhibitors. Potentiodynamic polarization curves indicated that both the decylamide of tyrosine and glycine acted primarily as anodic type inhibitors, whereas the
decylamide of alanine and valine were of the cathodic type. Thermodynamic parameters and Flory-Huggins adsorption isotherms described the experimental findings. The number of active sites, equilibrium constant, enthalpy and change of free energy were computed for all inhibitors studied. This information suggested that organic molecules were adsorbed and displaced water molecules from the steel surface. X-ray photoelectron spectroscopy confirmed that species of N, C and O interacted with the steel to form a continuous protective film. The effect of cysteine on the corrosion of low carbon steel in H₂SO₄ solution was studied using electrochemical and scanning electron microscopy (SEM) techniques [97]. Electrochemical impedance spectroscopy (EIS) results reveal that the presence of cysteine at low concentrations (0.1-0.5 mmoL⁻¹) promoted the carbon steel corrosion process, whereas an inhibiting effect was observed at higher concentrations (1.0-5.0 mmoL⁻¹), which was enhanced on deaeration of the test solution. Polarization results revealed that cysteine actually inhibited the cathodic process at all concentration but exerted a stimulating effect on the anodic metal dissolution reaction. Despite the cathodic inhibiting effect, the polarization resistances at low cysteine concentrations were less than that in the blank acid. This suggests that anodic reaction was the predominant influence determining the corrosion rates in the presence of cysteine.

The adsorption characteristics of methionine on mild steel surface in 0.5 M H₂SO₄ solution at a temperature of 25 ± 0.1 °C have been investigated using electrochemical impedance spectroscopy, polarization resistance measurement and polarization curves measurement techniques [108]. Constant phase element (CPE) has been used instead of double layer capacitance (Cdl) in circuit that models the double layer to represent the capacitive semicircle depression in the complex plane plots. The
values of polarization resistance ($R_p$) from polarization resistance measurement technique agreed well with the sum of the distinct resistances (solution resistance, $R_s$ and charge transfer resistance, $R_{ct}$) from impedance technique. Adsorption of methionine on mild steel surface was found to obey the Langmuir adsorption isotherm with a $\Delta G^{\circ}_{\text{ads}}$ of -32 kJ/mol. The behavior of L-methionine as a green organic inhibitor was studied using mild steel rotating disc electrode [119]. Electrochemical impedance spectroscopy (EIS) and polarization measurements were carried out in the absence and presence of inhibitor in 1 M H$_2$SO$_4$ solution under static conditions and at different rotation speeds; the inhibitor concentration was $5\times10^{-3}$ M in all tests. The open circuit potentials (OCP) versus time were measured. At all studied rotation speeds; it was found that the OCP shifted toward more positive potentials as the rotation speed increased. This behavior could be attributed to the enhanced mass transport of inhibitor molecules from bulk to the metal surface in high rotation rates.

Morad et al [120] investigated the effect of five S-containing amino acids namely N-acetylcysteine, cysteine, S-benzylcysteine, cystine, methionine on the corrosion of mild steel in 5% sulfamic acid solution at 40 °C using linear polarization $R_p$, potentiodynamic polarization curves and EIS techniques. The compounds are effective inhibitors and the inhibition efficiency follow the order: N-acetylcysteine (ACC) > cysteine (RSH) > S-benzylcysteine (BzC) > cystine (RSSR) $\equiv$ methionine (CH$_3$SR). The inhibitors affect the anodic dissolution of steel by blocking the anodic sites of the surface. EIS measurements indicated that charge transfer is the rate determining step in the absence and presence of the inhibitors and the steel/solution interface can be represented by the equivalent circuit $R_s (R_{ct} Q_{dl})$. Adsorption of RSH, CH$_3$SR and RSSR follows the Langmuir model while the Temkin isotherm describes
the adsorption of ACC and BzC. From the application of Flory-Huggins isotherm, the number of water molecules displaced by the adsorbing inhibitor molecules was estimated. The potential of zero charge \( pzc \) of mild steel without and with the inhibitors is calculated and the mechanism of corrosion inhibition is discussed in the light of the molecular structure. The inhibition effect of L-cysteine as environmental friendly corrosion inhibitor for XC18 carbon steel in stirred 2 N sulphuric acid was investigated by electrochemical techniques at 30-60 \( ^\circ \)C [99]. The impedance measurements showed that the inhibition efficiency increased with increase of inhibitor concentration reaching more than 84% at 500 mg/L; L-cysteine act as mixed type inhibitor and the adsorption followed the Langmuir isotherm. The values of adsorption free energy (\( \Delta G_{\text{ads}}^{\circ} \)) and activation energies (\( E_a \)) reveal a physical adsorption of the inhibitor on the steel surface. Amino acid L-Leucine was evaluated as a potential corrosion inhibitor for mild steel in 1 N H\(_2\)SO\(_4\) by galvanostatic polarization and potentiostatic polarization techniques [121]. The electrochemical results were supplemented by scanning electron microscopy (SEM) and infrared studies (IR). The electrochemical polarization results showed that L-Leucine is most effective at \( 10^{-4} \) M concentration at room temperature. The efficiencies were found to decrease with decrease in concentration and increase in temperature. Electrochemical results showed that L-Leucine acts as mixed type of inhibitor (blocks the cathodic and anodic sites to same extent) which is evident from insignificant shift of open circuit potential. The potentiostatic polarization data shows that inhibitor is passivating type. Alternating current (AC) impedance measurements of cystine adsorption at mild steel/sulphuric acid interface in presence of various concentrations of cystine have been carried out in the 100 kHz-10 mHz frequency range [122]. The results revealed
that cystine is a good and effective inhibitor for mild steel corrosion in 0.5 M H₂SO₄.

The percent inhibition efficiency changes with cystine concentration. Changes in impedance parameters indicated the adsorption of cystine on the mild steel surface, which was verified by SEM and atomic force microscope (AFM) photographs. The SEM and AFM photographs showed that the inhibition is due to the formation of the film on the metal surface through adsorption of cystine molecules. Adsorption of cystine on mild steel surface was found to obey the Langmuir adsorption isotherm with a standard free energy of adsorption $\Delta G^o_{\text{ads}}$ of -33.2 kJ/mol. Energy gaps for the interactions between mild steel surface and cystine molecule were found to be close to each other showing that cystine owns the capacity to behave as both electron donor and electron acceptor.

The inhibition effects of two amino acids methionine and tyrosine on the corrosion of iron in 0.1 M HCl solution was studied using electrochemical, FTIR and quantum chemical techniques [123]. The highest inhibition efficiency of 97.8% was determined at 100 ppm of methionine. The inhibition efficiency of the compounds was found to increase with increase in their concentration. Methionine was found to be more effective than tyrosine. The adsorption of the inhibitors accords with the Langmuir adsorption isotherm. Quantum chemical calculations performed for methionine and tyrosine, as well as, their protonated structures, corroborate that both theoretical and experimental inhibition effect of methionine is better than that of tyrosine.

The inhibition behavior of low carbon steel in 1 M HCl by L-tryptophan in the temperature range of 298-328 K was investigated using weight loss experiment and
Tafel polarization curves [102]. All the experimental results showed that L-tryptophan has excellent corrosion inhibition performance and the most effective concentration of inhibitor is $1 \times 10^{-2}$ mol/L. The Tafel polarization curve results indicate that L-tryptophan acts more as a cathodic than anodic inhibitor. The adsorption of L-tryptophan on the surface of low carbon steel obeys the Langmuir adsorption isotherm. The adsorption behavior of L-tryptophan at Fe surface was also investigated by the molecule dynamics simulation method and density functional theory. The results indicated that the L-tryptophan could adsorb firmly on the Fe surface through the indole ring with $\pi$-electrons and nitrogen/oxygen atom with lone-pair electrons in its molecule. Fu et al [124] investigated the corrosion inhibition behavior of four selected amino acid namely, L-cysteine, L-histidine, L-tryptophan and L-serine on mild steel in deaerated 1.0 M HCl electrochemically by Tafel polarization and electrochemical impedance spectroscopy methods and computationally by the quantum chemical calculation and molecular dynamics simulation. The order of inhibition efficiency of these inhibitors follows the sequence: L-tryptophan > L-histidine > L-cysteine > L-serine. The quantum chemical calculations were performed to characterize the electronic parameters which are associated with inhibition efficiency. The molecular dynamics simulations were applied to find the equilibrium adsorption configurations and calculate the interaction energy between inhibitors and iron surface. Results obtained from Tafel and impedance methods are in good agreement. The electrochemical experimental results are supported by the theoretical data. Amin et al [125] investigated three selected amino acids namely, alanine (Ala), cysteine (Cys) and S-methylcysteine (S-MCys) as safe corrosion inhibitors for iron in aerated stagnant 1.0 M HCL using Tafel polarization and impedance measurements.
Results indicate that alanine acts mainly as a cathodic inhibitor, while cysteine and S-methylcysteine function as mixed-type inhibitors. Cysteine, which contains a mercapto group in its molecular structure, was the most effective among the inhibitors tested, while alanine was less effective than S-methylcysteine. The low inhibition efficiency recorded for S-methylcysteine compared with that of cysteine was attributed to steric effects caused by the substituent methyl on the mercapto group.

The inhibition and adsorption potentials of four amino acids namely cysteine, glycine, leucine and alanine for the corrosion of mild steel in 0.1 M HCl solution were investigated using experimental and quantum chemical approaches [126]. The experimental study was carried out using gravimetric, gasometric, thermometric and FTIR methods while the quantum chemical study was carried out using semi-empirical, ab-initio and quantitative structure activity relation (QSAR) methods. The results obtained indicated that various concentrations of the studied amino acids inhibited the corrosion of mild steel in HCl solution through physiosorption. The inhibition potentials of the inhibitors decreased in the order: cysteine > leucine > alanine > glycine. The adsorption of the inhibitors on mild steel surface was found to be exothermic, spontaneous and supported the Langmuir adsorption model. Results obtained from quantum chemical studies showed excellent correlations between quantum chemical parameters and experimental inhibition efficiencies. Correlations between the experimental inhibition efficiencies and theoretical inhibition efficiencies were also excellent. Fu et al [127] investigated the inhibition effect of L-Cysteine (CYS) and its derivatives including N-acetyl-L-cysteine (NACYS), N-acetyl-S-benzyl-L-cysteine (NASBCYS), and N-acetyl-S-hexyl-L-cysteine (NASHCYS) as green chemical for mild steel in 1 M HCl solution. Weight loss method and Tafel
polarization measurement were performed to determine the corrosion parameters and inhibition efficiencies. Experimental results showed that these compounds suppressed both anodic and cathodic reaction, and the inhibition efficiency of the four inhibitors followed the order: $N$-acetyl-$S$-benzyl-\textit{L}-cysteine > $N$-acetyl-$S$-hexyl-\textit{L}-cysteine > $N$-acetyl-\textit{L}-cysteine > \textit{L}-cysteine. The relationships between quantum chemical parameters and corrosion inhibition efficiency were discussed. Molecular dynamics method was used to simulate the adsorption behavior of each inhibitor in the solvent. The results showed that these four inhibitors can adsorb on mild steel surface by donor acceptor interactions between lone-pair electrons of heteroatoms/\pi-electrons of aromatic ring and vacant d-orbital of iron. Abdel Ghanyl et al [128] investigated the inhibition effect of four amino acids glycine, leucine, arginine and valine on the corrosion of 316L stainless steel in 1.0 M H\textsubscript{2}SO\textsubscript{4} by studying open-circuit potential and potentiodynamic polarization measurements. Corrosion parameters were determined by extrapolation of the cathodic and anodic Tafel region. Glycine, leucine and valine inhibited the corrosion process, whereas the arginine accelerated the corrosion phenomenon. The presence of arginine at high concentration turns the surface of 316L stainless steel electrochemically active, probably dissolving the passivation layer and promoting the stainless steel anodic dissolution. Shenawy [129] investigated the corrosion inhibition of Lysine on SS 316L in 0.1 M H\textsubscript{2}SO\textsubscript{4} solution using open circuit potential measurements, potentiodynamic measurements and scanning electron microscopy (SEM) techniques. The open circuit potential becomes more positive with increasing the concentration of lysine. Potentiodynamic polarization measurements showed that the presence of lysine affect the cathodic process and decrease the corrosion current to a greater extent and corrosion potential
shifts towards more negative values. Results revealed clearly that lysine is a good cathodic type inhibitor for SS 316L in 0.5 M H2SO4. The effect of tryptophan on the corrosion behavior of low alloy steel in sulfamic acid which is widely used in various industrial acid cleaning applications was studied by electrochemical methods (electrochemical impedance spectroscopy; EIS and the new technique electrochemical frequency modulation; EFM) as well as gravimetric measurements [130]. It was shown that the inhibition property of tryptophan was due to the electrostatic adsorption of the protonated form of tryptophan on the steel surface. Adsorption of the inhibitor molecule, onto the steel surface followed the Temkin adsorption isotherm. All of the obtained data from the three techniques were in close agreement, which confirmed that EFM technique can be used efficiently for monitoring the corrosion inhibition under the studied conditions. Three selected amino acids, namely serine, threonine and glutamine were tested as corrosion inhibitors for cold rolled steel (CRS) in 1.0 M HCl solutions at 283-333 K by Chemical (weight loss) and electrochemical (Tafel polarization) methods [131]. Electrochemical frequency modulation (EFM), a non-destructive corrosion measurement technique that can directly give values of corrosion current without prior knowledge of Tafel constants, was also employed. Experimental corrosion rates determined by the Tafel extrapolation method were compared with those obtained by EFM technique and the weight loss method. Morphologies of the corroded and the inhibited surfaces were studied by means of atomic force microscopy (AFM) and scanning electron microscopy (SEM). Tafel plots showed that the three tested amino acids act as mixed-type inhibitors. The amino acids appeared to function through adsorption following
the Temkin adsorption isotherm model. Glutamine was found to inhibit corrosion of steel more effectively than serine and threonine.

In addition to iron base alloys amino acids have also been exploited as corrosion inhibitor for non ferrous metals like Cu, Al, Pb and their alloys [132-143]. Inhibition effect of $\alpha$-amino acids namely, arginine, histidine, glutamine, aspargine, alanine and glycine on the inhibition of pitting corrosion of Al in 0.1 M NaCl solution was studied by potentiodynamic technique [132]. All the studied inhibitors shifted the pitting potential ($E_p$) and the protection potential ($E_{pp}$) towards more noble values. The order of effectiveness of the inhibitors was arginine > histidine > glutamine > aspargine > alanine > glycine. Abdallah and Atia [133] reported the corrosion parameters for the corrosion of admiralty brass electrode in 0.1 M H$_2$SO$_4$ in the presence of four amino acids glycine, L-phenyl alanine and L-tyrosine and L-histidine by carrying out weight loss and polarization studies. The inhibition efficiency of these compounds was found to depend on the concentration and their chemical structure. The inhibition efficiency was found in the order of histidine > tyrosine > phenyl alanine > glycine. Ashassi-Sorkhabi et al [95] investigated the inhibition effect of amino acids alanine, leucine, valine, proline, methionine, and tryptophan towards the corrosion of aluminum in HCl and H$_2$SO$_4$ by using weight loss, linear polarization and SEM techniques. The investigated amino acids acted as good inhibitors for the corrosion of aluminum in HCl and H$_2$SO$_4$ solution. The adsorption of used amino acids on aluminum surface followed Langmuir and Frumkin isotherms. The inhibition effect of two amino-acid compounds, DL-alanine and DL-cysteine, on copper corrosion in an aerated 0.5 mol/L HCl solution was studied by weight-loss measurements, potentiodynamic polarization curves, and electrochemical impedance
spectroscopy [93]. A conventional benzotriazole (BTA) inhibitor was also tested for comparison. DL-cysteine was shown to be the most effective inhibitor among the tested inhibitors. Potentiodynamic polarization results revealed that both the DL-alanine and DL-cysteine acted as an anodic inhibitor; however, DL-cysteine, in particular, was more effective, as it strongly suppressed anodic current densities. The improved inhibition efficiency of DL-cysteine in the 0.5 mol/L HCl solution was due to its adsorption on the copper surface via the mercapto group in its molecular structure. Morad and Hermas [134] reported the influence of amino acids glycine, serine, methionine and vitamin C and some of their binary mixtures on the anodic dissolution of tin in 3.5% NaCl solution. The inhibitors were used in the concentration range of 25-100 mM. The studies were carried out by means of potentiodynamic and impedance techniques. The corroded tin surface was examined by SEM. The results indicated that the passive behavior of tin is greatly improved by the presence of 50-100 mM glycine and methionine while such improvement is achieved only at 100 mM serine. Both cysteine and vitamin C showed aggressive action. The pitting corrosion of aluminium alloy 7075 in 0.05 M NaCl solution at pH values of 4, 5, 7 and 8 was studied by potentiostatic method [135]. It was found that addition of $10^{-2}$ M hydroxy carboxylic acids or amino acids to NaCl solutions shifted $E_{\text{pit}}$ values to noble directions. Amino acids were more effective in shifting $E_{\text{pit}}$ values to nobler directions in acidic solutions whereas hydroxy carboxylic acids were more effective in shifting $E_{\text{pit}}$ values to nobler directions in neutral or basic solutions. Moretti and Guidi [136] investigated the use of tryptophan as a copper corrosion inhibitor in 0.5 M aerated H$_2$SO$_4$ in the temperature range 20-50 °C. The effectiveness of the inhibitor was assessed through potentiodynamic (at 1 h, 72 h, 6 months), spectrophotometric (72 h
tests) and gravimetric (72 h tests) tests. At 20-50 °C (1 h tests) the tryptophan adsorption followed Bockris-Swinkels’ isotherm. The tryptophan even underwent photodegradation, but this did not affected the inhibition percentage which was 80% for the solutions kept in the dark as well as those kept in light.

The environmentally safe corrosion inhibitions of lead in aqueous solution with different pH (2, 7 and 12) were investigated by Helal et al [137]. The corrosion rate was calculated in the absence and presence of the corrosion inhibitor amino acids using polarization and impedance technique. Corrosion inhibition efficiency up to 87% was recorded with glutamic acid in neutral solutions. The experimental impedance data were fitted to theoretical values according to an equivalent circuit model to explain the behavior of the metal under different conditions. The corrosion inhibition process was found to depend on the adsorption of the amino acid molecules on the metal surface. The free energy of adsorption of glutamic acid on Pb was found to be equal to -2.9 kJ/mol, which reveals that the inhibitor is physically adsorbed on the metal surface. The inhibition effect of five amino acids namely, valine, glycine, arginine, lysine and cysteine on the corrosion of copper in nitric solution was studied by using weight loss and electrochemical polarization measurements [138]. Valine and glycine accelerate the corrosion process but arginine, lysine and cysteine inhibit the corrosion phenomenon; cysteine was the best inhibitor attaining IE of 61% at 10^{-3} M. Ranjana et al [139] investigated the inhibition effect of three amino acids glycine, L-aspartic acid, L-glutamic acid and their benzenesulphonyl derivatives namely, N-benzenesulphonyl glycine, N-benzenesulphonyl L-aspartic acid and N-benzenesulphonyl L-glutamic acid on the corrosion of brass in 0.6 M aqueous sodium chloride solution studying by potentiodynamic polarization and electrochemical
impedance spectroscopy. It was shown that the inhibition efficiency of these compounds increases in the order of L-glutamic acid > L-aspartic acid > glycine for amino acids and same trend is followed for benzenesulphonyl derivatives. The inhibition efficiency of N-benzenesulphonyl L-glutamic acid with $4 \times 10^{-5}$ M concentration is the highest, which reaches 81.2-85.5%. It has been observed that introduction of $\text{C}_6\text{H}_5\text{SO}_2^-$ group increases the inhibition efficiency of the amino acids by 14-33% due to $\pi$ electron contribution of the benzene ring and presence of more active adsorption sites. Helal and Badawy [140] studied the corrosion inhibition of Mg-Al-Zn alloy in stagnant naturally aerated chloride free neutral solutions using amino acids as environmentally safe corrosion inhibitors. The corrosion rate in the absence and presence of the corrosion inhibitor was calculated using the polarization technique and electrochemical impedance spectroscopy. It was found that Phenyl alanine has corrosion inhibition efficiency up to 93% at a concentration of $2 \times 10^{-3}$ mol dm$^{-3}$. The free energy of the adsorption process revealed a physical adsorption of the inhibitor molecules on the alloy surface. Helal [141] showed the corrosion inhibition behavior of Mg-Al-Zn alloy by different electrochemical techniques in neutral solutions containing chloride ions at different concentrations. The corrosion rate was calculated in the absence and presence of methionine as an environmentally safe corrosion inhibitor using polarization and impedance techniques. The results reveal that methionine inhibits the corrosion reaction by adsorption onto the metallic surface. Polarization results revealed that methionine acts as an anodic inhibitor. The inhibitory effects of tryptophan on the corrosion of Aluminium alloy AA 2024 in 1 M HCl, 20% (wt. %) CaCl$_2$, and 3.5% (wt. %) NaCl solutions were investigated via polarization techniques, electrochemical impedance spectroscopy, and weight loss
methods [142]. The scanning electron microscope technique was employed to observe
corrosion morphology. The results suggest that AA 2024 was corroded in these three
corrosive media to some extent and that tryptophan can significantly inhibit the
corrosion of aluminum alloys. The inhibition efficiency increased with increasing
concentrations of tryptophan, and the best inhibition efficiency exhibited was about
87% in 1 M HCl solution with 0.008 M tryptophan. Tryptophan acted as a cathodic
corrosion inhibitor and affected the hydrogen evolution reaction, which was the main
electrode reaction in the 1 M HCl solution. In solutions with 20% CaCl₂ and 3.5%
NaCl, tryptophan was adsorbed onto anodic areas, thus increasing the activation
energy of the interface reaction as an anodic corrosion inhibitor. The Dmol³ program
of Material Studio 4.0 was used to obtain the optimized geometry of the tryptophan
inhibitor and some quantum-chemical parameters. Front orbital distributions and
Fukui indices indicate that the molecular active reaction zones were located in the
indole ring of tryptophan. Abdel Rahman et al [143] reported a comparative study of
different types of amino acids namely, proline, cysteine, phenyl alanine, alanine,
histidine and glycine as corrosion inhibitors for copper corrosion in 8 M phosphoric
acid at different temperatures. Potentiodynamic polarization and rotation techniques
were used during the experiments. It is shown that amino acids have strongest
inhibitive effects that provide good protection to copper surface against corrosion in
acid solutions. Adsorption of amino acids on copper surface, in 8 M phosphoric acid
solution, follows Temkin adsorption isotherm model. Quantum chemical parameters
were calculated using semiempirical PM6 method to find a good correlation with the
inhibition efficiency. A good correlation was found between the theoretical
calculations and experimental observations.
1.7 Corrosion Inhibition Using Surfactants

Surfactants also called surface active agents are molecules composed of a polar hydrophilic group, the “head”, attached to a non-polar hydrophobic group, the “tail”. The hydrophobic portion is usually a branched or straight hydrocarbon chain containing 6-22 carbon atoms. The hydrophilic portion can be ionic (cationic, anionic), zwitterionic, or nonionic depending on the nature of their head groups. In aqueous solution, the hydrophobic chain interacts weakly with the water molecules, whereas the hydrophilic head interacts strongly via dipole or ion-dipole interactions. This strong interaction between water and ‘head-group’ renders the surfactant soluble in water. Surfactants can reduce surface and interfacial tensions by accumulating at the interface of immiscible fluids and increase the solubility, mobility, bioavailability and subsequent biodegradation of hydrophobic or insoluble organic compounds.

Depending on the charge of head groups, the surfactants are classified as anionic, cationic, nonionic and amphoteric (zwitterionic) surfactants. Anionic surfactants are dissociated in water into an amphiphilic anion, and a cation, which is, in general, an alkaline metal ion (Na\(^+\), K\(^+\)) or a quaternary ammonium. This class of surfactants is widely used in industrial applications due to their relatively low cost of manufacture. Most commonly used anionic groups are alkylbenzenesulfonates, lauryl sulfate, lignosulfonates, fatty acid soaps, etc. In cationic surfactants, cation is the surface-active species. The quaternary ammonium salts are the main compounds belonging to this class of surfactants. A very large proportion of this class of molecules corresponds to nitrogen compounds such as fatty amine salts and quaternary ammoniums, with one or several long chain of the alkyl type, often
coming from natural fatty acids. Nonionic surfactant does not have any surface charge and have either a polyether or a polyhydroxyl unit as the non-polar group. In the majority of the nonionics, the polar group is a polyether consisting of oxyethylene units, prepared by the polymerization of ethylene oxide. They can be mixed with other types of surfactants, e.g., anionic or cationic, to enhance their properties and reduce surfactant precipitation [144, 145]. This class of surfactants has substantially lower critical micelle concentrations (CMC) than the corresponding ionic surfactants and continues to be dominated by ethylene oxide adducts of alkylphenols and fatty alcohols. The amphoteric or zwitterionic surfactants contain both cationic and anionic groups and show good compatibility with other surfactants. Some amphoteric surfactants are insensitive to pH, whereas others are cationic at low pH and anionic at high pH with an amphoteric behavior at intermediate pH. Some of the examples are betaines, aminoacids, sulfobetaines and phospholipids. A new class of recently developed surfactants called Gemini or dimeric surfactants have two hydrophilic (chiefly ionic) groups and two tails per surfactant molecule. These twin parts of the surfactants are linked by a rigid or flexible spacer group of varying length (most commonly a methylene spacer or an oxyethylene spacer). Gemini surfactants exhibit remarkably a number of superior properties when compared to single chain conventional surfactants. They possess lower values of CMC, better wetting properties, increased surface activity and lower surface tension at the CMC, enhanced solution properties such as hard-water tolerance and lower Krafft points [146-150].

The promising potential application of surfactants as corrosion inhibitors in acidic media has been widely studied during the last two decades [151-161]. The corrosion inhibition by surfactant molecules is related to their remarkable ability to
influence the properties of surfaces and interfaces. In general, in aqueous solution the inhibitory action of surfactant molecules may be due to the physiosorption (electrostatic) or chemisorption onto the metallic surface, depending on the charge of the solid surface. The degree of their adsorption on metal surfaces depend on the nature of the metal, the mode of adsorption, chemical structure of the surfactant, the metal surface condition, and the type of corrosion media [162]. The adsorbed surfactants molecules form a monolayer or bilayer, hemimicelles or admicelles and prevent the acids to attack the surfaces. Surfactant inhibitors have many advantages over traditional corrosion inhibitors. For example, they are easily produced, are economical and possess high inhibition efficiency and low toxicity [163-165]. The adsorption of a surfactant markedly changes the corrosion resisting property of a metal, and for these reasons, studies of the relation between adsorption and corrosion inhibition are of considerable importance [166-169] The adsorption behavior of surfactants at the solid/solution interface is somewhat similar to that at the gas/solution interface although the latter is more complicated than the former [170, 171]. Surfactants have widely been used for inhibition of pitting corrosion of stainless steel [172], as corrosion inhibitors for carbon steel pipelines in oil fields, aluminum alloys and mild steel [158, 173, 174]. A number of investigators were able to reduce the steel corrosion in acidic media [175-180] by means of the surfactants. The surfactant can be used either alone or in mixture with other compounds to improve their performance as inhibitors.

The ability of a surfactant molecule to adsorb is generally directly related to its ability to aggregate and to form micelles. Micelles are spontaneously formed clusters of surfactant molecules (typically 40 to 200), whose size and shape are governed by
geometric and energetic considerations. Consequently, the CMC is an important parameter in determining the effectiveness of a surfactant as a corrosion inhibitor. The concentration above which the surfactant molecules aggregate to form micelles is called critical micelle concentration or simply CMC. When the concentration of surfactant adsorbed on the solid surface is high enough, organized structures (hemi-micelles such as bi- or multilayer) are formed, which decrease the corrosion reaction by blocking the metallic surface [156, 179, 181]. Below the CMC, individual surfactant molecules or monomers tend to adsorb on exposed interfaces, so interfacial aggregation reduces surface tension; this is related to corrosion inhibition. Above the CMC, the surface becomes covered with more than one monolayer and forms a protection layer on the metal surface. Thus any additional surfactant added to the solution above the CMC will lead to the formation of micelles or multiple adsorbed layers on the surface. Consequently, the surface tensions, and also the corrosion current density, are not altered significantly above the CMC. Therefore, an efficient surfactant inhibitor is one that aggregates or adsorbs at low concentrations. In general, lower the CMC of the surfactant the greater is its tendency to adsorb at the solid surface [182-189]. Various factors effects the CMC values e.g., temperature, the length of the hydrocarbon tail, the nature of the counter ions and the existence of salts and organic additives, and thus amphiphiles have characteristic CMC values under given conditions [190, 191].

1.8 Synergism Consideration in Corrosion Inhibition

The word synergism is derived from the Greek word synergos meaning acting together. Synergism or mutual increase is a combined action of compounds greater in
total effect than sum of individual effects [192-196]. It is one of the most important
effects in inhibition process and serves as basis for modern corrosion inhibiting
formulations [197, 198]. Synergism of corrosion inhibitors is either due to interaction
between constituents of the inhibitor or due to interaction between the inhibitor and
one of the ions present in aqueous solution [199-201]. It is a nonlinear effect resulting
in non-additive efficiencies of inhibitor components. In most cases, the mechanism of
synergism differs from the mechanism of the individual inhibitors. It is, therefore,
necessary for corrosion researchers to discover, explore and use synergism in the
complicated corrosive media. By taking advantage of synergism the amount of
inhibitor applied can be decreased or an environmental friendly but less effective
corrosion inhibitor can be used more effectively.

The addition of halide ions to organic compounds has shown synergistic effect
and resulted in improved inhibition efficiency of many organic compounds [197, 202-
205]. However, there remains relatively few works directed towards the synergistic
between the different amino acids and other compounds. Oguzie et al [98] found that
inhibition efficiency of methionine synergistically increased in the presence of KI,
with an optimum KI/methionine ratio of 1/1. Ismail [206] reported that the maximum
inhibition efficiency of cysteine can be achieved at about 84%; the presence of Cu^{2+}
ions synergistically increases the inhibition efficiency to 90% in neutral and acidic
chloride solution. The influence of Zn^{2+} ions on inhibition efficiency of methionine
for copper corrosion in 0.5 M HCl has been studied by cyclic voltammetry,
electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization
techniques [207]. Methionine has shown limited inhibiting properties for copper
corrosion in 0.5 M HCl. However, the presence of Zn^{2+} ions synergistically increases
the inhibition efficiency to 92%. Results obtained from potentiodynamic polarization and impedance measurements are in good agreement. The corrosion protection of copper by glutamic acid, cysteine, glycine and their derivative (glutathione) in 0.5 M HCl solution has been studied by electrochemical impedance spectroscopy and cyclic voltammetry [208]. The inhibition efficiency of the organic inhibitors on copper corrosion increase in the order: glutathione > cysteine > cysteine + glutamic acid + glycine > glutamic acid > glycine. Maximum inhibition efficiency for cysteine reaches about 92.9% at 15 mM concentration level. The glutathione can give 96.4% inhibition efficiency at a concentration of 10 mM. The intramolecular synergistic effect of glutamic acid, cysteine and glycine moieties in glutathione is attributed to the lower energy of the lowest unoccupied molecular orbital (E_LUMO) level and to the excess hetero-atom adsorption centers and the bigger coverage on the copper surface.

Though the synergistic influence of halide ions on different organic compounds has been adequately investigated there remains relatively few works directed towards the synergistic between the different organic compounds and surfactants [209, 210]. In a very recent paper the inhibition behavior of methionine combined with cetrimonium bromide (CTAB) and cetylpyridinium bromide (CPB) for Cu corrosion in 0.5 M HCl solution has been reported. It has been shown that combination of methionine with CTAB or CPB provides strong synergistic inhibition effect [211].
1.9 STATEMENT OF THE WORK PRESENTED IN THE THESIS

The corrosion of mild steel is a subject of fundamental, academic and industrial concern and has received considerable attention during the last few decades. The use of inhibitors is one of the most effective practical and economic methods to protect metallic surfaces against corrosion in aggressive acidic media. Mineral acids are widely used in various industries for pickling of steel at elevated temperatures up to at 60 °C. This technique besides being used to remove corrosion scales from steel surface without causing acid attack of the bulk metal is also effectively applied in cleaning of industrial equipment and acidization of oil well. Most of the efficient pickling inhibitors are organic compounds containing hetero atoms such as sulfur, nitrogen, oxygen, phosphorus, and multiple bonds or aromatic rings in their structures. However, most of the organic compounds used as corrosion inhibitors are toxic and hazardous to both human beings and the environment and needs to be replaced by nontoxic, environment friendly compounds. As a result, the current research trend is towards the development of nontoxic, economical and more environmentally safe green chemicals as corrosion inhibitors.

It has been shown by a number of investigators that some amino acids can act as corrosion inhibitors, which has generated an increasing interest in these compounds. Amino acids are attractive as corrosion inhibitors because they are relatively easy to produce with high purity at low cost and are nontoxic, biodegradable and completely soluble in aqueous media. Surfactants, which have a remarkable ability of influencing the surfaces and interfaces, have shown a significant role in the inhibition of acid corrosion of mild steel. The surfactant can be used either alone or in mixture with other compounds to improve their performance as inhibitors.
A survey of literature indicates that the corrosion inhibition effect of amino acids in presence of surfactants perhaps has yet not been reported. Amino acids are likely to interact with the surfactants to form complex structure and help to adhere to mild surface and thus offer greater resistance to corrosion.

The work presented in this thesis deals with the corrosion inhibition behavior of different amino acids separately and in combination with very low concentration of the anionic and cationic surfactants on mild steel in 0.1 M \( \text{H}_2\text{SO}_4/\text{HCl} \) solutions. The aim of the surfactants addition was to improve the corrosion inhibition behavior of environment friendly but less effective amino acids as corrosion inhibitor for mild steel corrosion in acidic medium. The concentration of surfactants was intentionally kept low so that the green nature of amino acids is least influenced. The amino acids considered for the investigations are L-Histidine (LHS), L-Tryptophan (LTP), L-Methionine (LMT), and L-Cystine (LCY). The surfactants subjected to investigation are anionic surfactant sodium dodecyl sulfate (SDS) and cationic surfactant cetyltrimethyl ammonium bromide (CTAB). The techniques used are weight loss measurements, potentiodynamic polarization measurements, scanning electron microscopy (SEM), atomic force microscopy (AFM) and thermodynamic/kinetic parameters. The breakup of the work contained in various chapters is as follows:

**Chapter I**

This chapter deals with the general introduction. The general introduction briefly describes the fundamentals of corrosion which includes the definition of corrosion and its importance, cost of corrosion and method of corrosion control. It presents an exhaustive literature survey exploiting green compounds including amino acids as corrosion inhibitor for mild steel in acid solutions. Except for some early
pioneering research papers, the thesis include literature survey from the selected research papers, reviews and reports published on the subject during the last three decades. Special emphasis has been laid to the work which has direct or indirect bearing on the studies presented in this thesis. It might be possible that some results of the important studies have been left unquoted quite inadvertently, yet there was absolutely no intension to undermine those works.

Chapter II

This chapter deals with the experimental details which includes the materials and methods used during the experimental work. The details of corrosion tests which have been undertaken to investigate the inhibition behavior of amino acids have also been explained in this chapter.

Chapter III

The work presented in this chapter deals with the corrosion inhibition behavior of L-histidine alone and in presence of surfactants, sodium dodecyl sulfate (SDS) and cetyltrimethyl ammonium bromide (CTAB) on mild steel in 0.1 M H₂SO₄ solution at 30-60 °C. The corrosion inhibition efficiency of L-histidine in acid solution alone and in presence of SDS and CTAB was determined using weight loss and potentiodynamic polarization measurements. The surface morphology of the mild steel before and after immersion in 0.1 M H₂SO₄ solution was also examined using SEM and AFM studies.

Chapter IV

This chapter deals with the corrosion inhibition behavior of L-tryptophan and surfactants additives on mild steel in 0.1 M HCl in the temperature range of 30-50 °C. The corrosion performance of additives on mild steel corrosion was investigated by
weight loss method and potentiodynamic polarization techniques. To determine if the corrosion inhibition is due to the formation of a protective film by adsorption of inhibitors scanning electron spectroscopy has also been performed on the corroded mild steel specimens. The mode of adsorption of inhibitor molecules on mild steel surface was also elucidated by determination of thermodynamic/kinetic parameters.

**Chapter V**

This chapter deals with the corrosion inhibition behavior of sulfur containing amino acid L-methionine with surfactants mixture. The corrosion behavior of mild steel in 0.1 M H₂SO₄ in absence and presence of different concentrations of L-methionine alone and in combination with surfactants SDS and CTAB, was studied in the temperature range of 30-60 °C using weight loss and potentiodynamic polarization measurements. The corrosion protection of mild steel by L-methionine and surfactants additives was confirmed by scanning electron spectroscopy and atomic force microscopy techniques and determination of thermodynamic/kinetic parameters.

**Chapter VI**

This chapter presents the results of the investigation concerning with the corrosion inhibition behavior of L-cystine and surfactant additives on mild steel corrosion in 0.1 M H₂SO₄ in the temperature range of 30-60 °C. The corrosion performance was investigated by weight loss measurements, potentiodynamic polarization measurements, scanning electron spectroscopy and atomic force microscopy techniques.
FIGURE CAPTIONS

Figure 1.1  Phase diagram of iron

Figure 1.2  Cathodic protection by impressed current

Figure 1.3  Cathodic protection by sacrificial anode

Figure 1.4  Schematic diagram showing protection range and optimum potential for anodically protecting an active-passive metal
Figure 1.1

Immunity Fe

Corrosion Fe^{2+}

Fe^{3+}

FeO_4^{2-}

Fe_2O_3.nH_2O
Figure 1.3

$3O_2 + 6H_2O \rightarrow 12OH^- + 4Al^{+++} + 12e^-$

Seawater

Aluminum

Anode connection

Protected Structure (Steel)
Figure 1.4