Introduction

1.1. Definition of Corrosion

Corrosion may be defined as the destruction of a metal by an electrochemical reaction with its surroundings. Corrosion is a natural process and is a result of the inherent tendency of metals to revert to their more stable compounds, usually oxides. Most metals are found in nature in the form of various chemical compounds called ores. In the refining process, energy is added to the ore, to produce the metal. It is the same energy that provides the driving force causing the metal to revert back to the more stable compound [1].

More attention is to be given to metallic corrosion due to:

1. An increased use of metals in many fields of technology – rare and expensive metals used in atomic energy field.
2. A more corrosive environment due to air and water pollution.
3. Slender dimensions used in metallic construction which do not tolerate corrosive attacks.

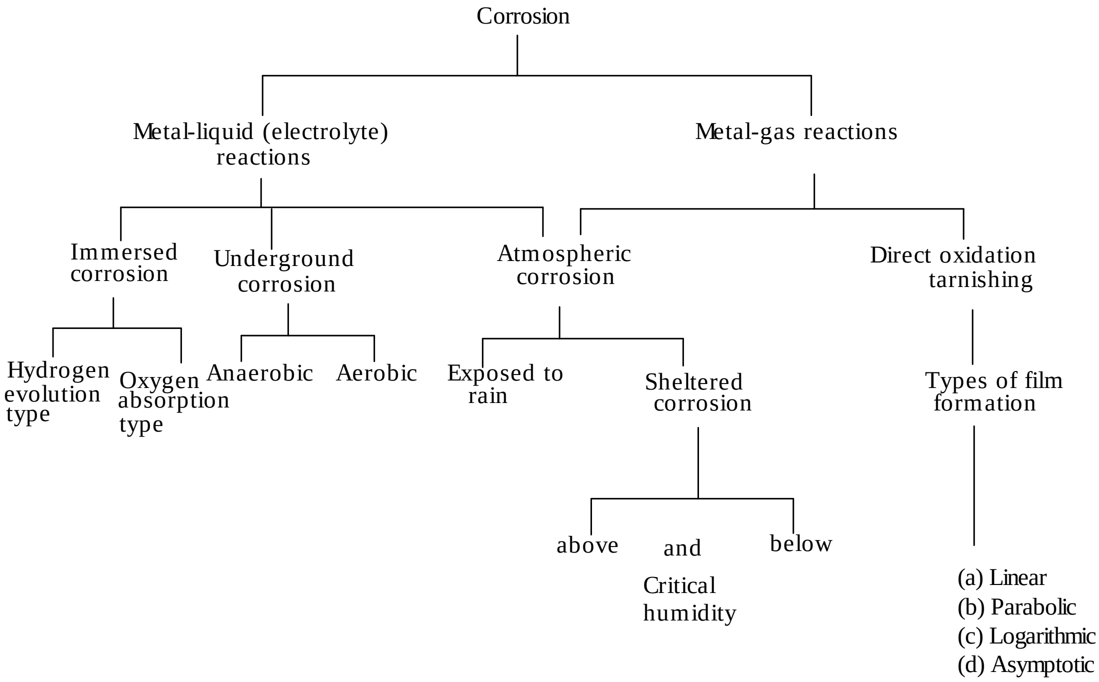
1.2. Classification of Corrosion

Corrosion has been classified in different ways. One way of classification is high temperature and low temperature corrosion; another way is wet and dry corrosion. The more preferred classification is based on mechanism, which falls into two types:

1. Electrochemical corrosion involving an interface in which anodic and cathodic areas can be distinctly identified or such identification is not possible.
2. Chemical corrosion which involves direct chemical reaction of the //metal.

The preferred classification is: Dry or chemical corrosion and wet or electrochemical corrosion.

1. Dry corrosion occurs in the absence of a liquid phase or above the dew point of the environment. Vapors and gases are usually coordinates; it is often associated with high temperature. An example is the attack of steel by furnace gases.
2. Wet corrosion occurs when a liquid is present in contact with the metal. This occurs in aqueous solutions or electrolytes. A common example is corrosion of steel by water.



1.3 Cost of Corrosion

It is justifiable that several crores of rupees are spent on research for controlling corrosion. Losses caused by corrosion could be direct or indirect.

1.3.1- Direct losses

1. Inability to use otherwise desirable materials.
2. Over design.
3. Replacement of corroded component or repair cost.
4. Cost of anticorrosive paints and other protective methods.

1.3.2 - Indirect losses

1. Contamination of the product.
2. Valuable part of the container getting corroded.
3. Adjacent equipment getting corroded.
4. Loss of production.
5. Safety (fire and explosion of toxic products).
6. Appearance (Unpleasant look of corroded materials).

1.4 - Factors Influencing Corrosion

The extent of corrosion and its nature largely depend upon the metal and the environment surrounding it. The important factors that influence the corrosion phenomenon are as follows:

a) Nature of the metal.
b) Environment.
c) Temperature
d) Concentration.
e) Nature of the corrosion product.
f) Electrode potential.
g) Aeration.
h) Agitation.
i) Hydrogen over voltage.
j) pH of the electrolyte.

1.5- Theories of Corrosion

The corrosion of metals in aqueous solution is an electrochemical process as established in the first half of the 19 Th centuries. Whitney [2] gave the most acceptable electrochemical theory. The other theories such as acid theory [3] chemical attack theory, colloidal theory [4,5] and biological theory [6] were proved to form a part of electrochemical theory.

1.5.1- Electrochemical theory

De La Rive developed Wollaston's electrochemical theory in 1830, confirmed by Ericson – Auren and Palmer in 1901. According to this theory, the heterogeneity on the metal surface causes the formation of galvanic cell, which is a prerequisite for corrosion. This suggests that ultra – pure metals are non – corrodible. For corrosion to occur there need not exist specially separated anodic and cathodic areas on the corroding metal. Oxidation and reduction reactions occur randomly over the metal surface and they tend to shift around on the entire surface causing uniform corrosion.

In anodic reaction, the oxidation of metal i.e., corrosion occurs, whereas in cathodic reaction a component of the corrosive environment is reduced. For corrosion to occur, the anodic and cathodic reactions should proceed at the same rate. The practical control methods available for the protection of metals against corrosion are diverse. They may be broadly classified based on:

a- Selection of materials.

b- Modification of metals.

c- Modification of design.

d- Modification of corrosive environment.

e- Modification of surface.

f- Modification of electrode potential of metal / corrosive medium.

these methods can be used individually.

1.5.1. A. DC methods

There are a number of DC methods available some of them are briefed below:

i. Tafel extrapolation method

From the plot of potential against log j, E_{corr}, j_{corr} and Tafel slopes (b_a and b_c) are obtained.

ii. Linear polarization method

Stern and Geary [7] have shown that there is a linear relationship between Current and potential when $\eta << 20mV$.

iii. Coulostastic method

This method is used to measure corrosion rates in high resistive media [8,9] in which Tafel extrapolation and linear polarization methods can not be applied.

iv. Charging curve method

At low corrosion rates, the approach of steady state during polarization is exceedingly slow due to the long time required for the double layer to get Charged at a vary low current. Inhibitor efficiency will be varying with time and hence difficult to obtain. Jones and Grene [10] have used this method for determining the R_p values.

v. Small amplitude cyclic Voltammetry (SACV)

SACV is used for measuring polarization resistance. Evaluation of corrosion rate [11] and double layer capacitance has been made for condensed systems.

1.5.1. B. AC methods

Impedance method

Among the various AC techniques, impedance is widely used to determine the double layer capacitance and charge transfer resistance. The term resistance and impedance both imply restriction to current flow. When dealing with DC only resistors produce this effect but in the case of AC both inductors and capacitors influence the electron flow.

Advantages of AC methods

i. AC impedance involves measurement of both capacitance and charge transfer resistance. This technique is very valuable.

ii. The perturbation is minimum and reduces the errors due to measurement.

iii. This method does not involve potential scan and therefore can be applied to low conductivity media. The impedance of the corroding system at various frequencies can be measured using lock-in amplifiers for high frequencies and fast Fourier Transform [12] technique for low frequencies.

1.5.2-Non- electrochemical theory

1.5.2. I. Weight loss method

The difference in weight of a metal due to corrosion is measured by exposing the metal specimen of known area to the environment for a known period of time, and then the corrosion rate calculated.

1.5.2. II. Electrical resistance method

On exposing a metal in the form of wire or rod to the environment there is reduction in cross section of the metal leading to an increase in electrical resistance. A change in the electrical resistance is the measure of the corrosion rate.

1.5.2. III. Gasometry

The volume of hydrogen gas evolved when a metal is treated with acid is measured at constant temperature and atmospheric pressure. From the volumes of hydrogen evolved the corrosion rate is calculated. The main disadvantage of these methods is that they are time consuming.

1.6- Corrosion Principles

Corrosion resistance or chemical resistance depends on the following:

i. Thermodynamic principles.
ii. Physical and chemical factors.
iii. Metallurgical factors.
iv. Electrochemical principles.

Thermodynamic and Electrochemical principles play a major role in determining the corrosion behavior of materials. Thermodynamics indicates the spontaneous direction of a chemical reaction. It is used to determine whether or not corrosion is theoretically possible.

Electrochemical principles are extensively used to determine the corrosion behavior of materials. Here the corrosion reaction can be represented by partial reaction such as metal oxidation and reduction of some reducible species of the environment both occurring simultaneously at equal rates the mixed potential [13] of the reaction. Corrosion reaction mainly occurs at the metal- environment interface.

The electrochemical nature of corrosion can be well understood by the dissolution of a metal in a strong acid with liberation of hydrogen; this is a typical redox reaction.

1-7- Corrosion Inhibitors.

The Protection of metals against corrosion can be achieved either with inhibitors or with passivating agents [14]. An inhibitor is any compound that suppresses corrosion, regardless of which electrochemical reaction it affects passivators, on the other hand, are defined as compounds that reduce the corrosion rate via a preferential retardation of the anodic reaction. In accordance with these definitions, an inhibitor may not be passivators, but every passivator is an inhibitor.

Inhihibitors can be used to great advantage for the protection of metals in many environments. However, it is important to note that inhibitors are generally specific to given metal and often specific to that metal in a particular environment and under particular service conditions. This specificity derives from the inhibitors mode of action inhibitors most useful in closed systems where the corrosive environment is either retained for long periods or recycled.

1.7.1- Classification of Inhibitors

Inhibitors are classified as acid, neutral, alkaline and vapour phase inhibitors depending upon the environment. Depending on the mechanism of inhibition, they are classified as cathodic, anodic and mixed type of inhibitors. Acid inhibitors can be further classified as inorganic and organic inhibitors.

Inorganic inhibitors are not of much importance for copper and its alloys.

Usually corrosion of metals and alloys in acidic, neutral and alkaline solutions can be inhibited by a large number of organic substances. In general, nitrogen, oxygen and sulphur containing compounds with a hydrocarbon part attached to the polar group are used as inhibitors. Triple bonded hydrocarbons, acetylenic alcohols, thioureas, sulfoxides, sulphides and mercaptans, aliphatic, aromatic or heterocyclic compounds and condensation products formed by the reaction between two different species such as aldehydes, amines and Schiff bases are mostly used. Schmitt **[15]** has reviewed the application of inhibitors for acid media. The performance of inhibitors depends on various factors like size, solubility, chemical structure, substituent effect, steric effect, carbon chain length, Hammett constant, molecular weight, basicity (pk), dipole moment, magnetic susceptibility, NMR shift, temperature, acid concentration, velocity of liquid flow, nature of metal and pH of the solution. In the case of mixture of inhibitors synergistic **[16]**, behaviours were reported. The study of various organic compounds in relation to their different aspects of inhibition in different environments has been reviewed by Sanyal **[17]**.

Some organic compounds like azoles, amines, thiourea etc. are adsorbed or chemisorbed on the surface of the metal and form a protective layer.

1.7.2- Applications of Inhibitors

The addition of inhibitors to minimize the corrosion rate is the other mainly used method, where the protection of the metal is achieved either by changing the characteristics of the electrolyte or by forming a protective passive film on the electrode surface. This can be done by adding certain anions like chromate, nitrate and phosphate to form a protective oxide film and by retarding the cathodic current density or by increasing the flade potential to more negative values and subsequently promoting the anodic process.

1.7.3- Mechanism of Inhibition

The following mechanisms are suggested to explain the phenomenon of corrosion inhibition.

1.7.3.1- Formation of a physical barrier and reduction in metal reactivity

The inhibitive action observed on the addition of organic compounds is due to the surface coverage (θ) by the compound owing to the adsorption or chemisorptions. The inhibitor may be selectively adsorbed onto the cathodic or anodic sites on the surface of the metal. This results in the decrease of cathodic or anodic reaction rate and thus corrosion is retarded. The adsorption on cathodic sites increases cathodic polarization and on anodic sites increases anodic polarization.

1.7.3.2- Change in the electrical double layer structure

According to the mechanism adsorbed organic molecules physic-ally block the sites on the metal surface resulting in the change of double layer structure at the metal/solution interface.

Though the action of inhibitors has been explained on the basis of various considerations, it is now generally accepted that organic compounds inhibit corrosion by adsorbing at the metal solution interface.

1. 8- Kinetics of Corrosion

The spontaneous dissolution of metal in the corrosive environment is facilitated by the parallel existence of a reduction reaction (cathodic process) other than reduction of metal ions. The rate and mechanism of corrosion process are determined by the kinetic factors that govern the individual anodic and cathodic reactions. The overall reaction is the sum of the partial reactions.

1.8.1- Activation controlled anodic and cathodic reactions

The formation of mixed potential of a corroding metal surface is illustrated in (Fig. 1.1) for corrosion reaction in which the partial reactions are activation controlled. The solid lines represent the net anodic and cathodic current for each reaction, while dashed lines represent forward and backward and part of each reaction [18]. The intersection of the solid lines gives the corrosion potential (E_{corr}) and corrosion current (j_{corr}). The intersection of the dashed lines gives the reversible potential and exchange current for the partial reactions.

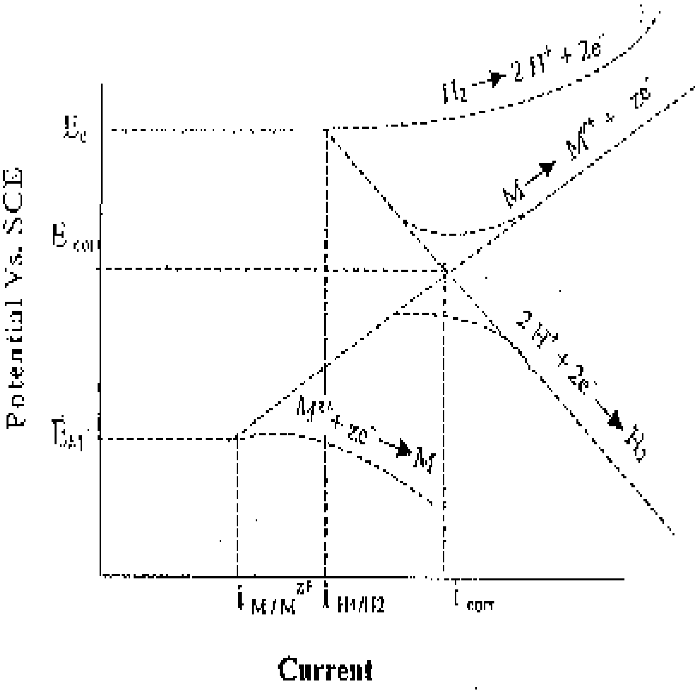


Fig. (1.1): Electrode kinetic behavior of pure metal (M) in acid solution (Drawn schematically)

The relationship between the over potential and current for a corroding system in which the anodic reaction is the metal dissolution.

$$\mathbf{M \longrightarrow M^{z+} + Z\,e^-} \qquad (1.1)$$

and the cathodic reaction is hydrogen evolution

$$\mathbf{2H^+ + 2\,e^- \longrightarrow H_2} \qquad (1.2)$$

Is given by Tafel equation:

$$\boldsymbol{\eta = \pm \beta \log j / j_0} \qquad (1.3)$$

Where η is over voltage (polarization), β is Tafel constant (β_a or β_c), j and j_0 are rate of oxidation and reduction in terms of current density and exchange current density respectively [19].

1.9- Mechanism of Corrosion Processes

All the corrosion processes involve the reduction reaction confined to hydrogen evolution or oxygen absorption and the oxidation reaction. i.e., anodic dissolution of the metal. Prediction of the rate of corrosion based on the hydrogen evolution is easier compared to oxygen absorption in which reaction takes place in many steps on the oxide-covered surface- a poor electron carrier. The anodic reaction which involves the movement of metal ions from the metal phase to the solution phase is also complicated which takes place through several steps like diffusion of ions on the surface, entry into solution phase as an intermediate step and solvation of ion as the final step. Five possible mechanisms for the corrosion of iron have been given [20-22].

1.10- Expression for Corrosion Rate

Weight loss measurement is the commonly used technique to measure the corrosion rate. The rate of corrosion is calculated from.

$$R = \frac{534\,W}{DAT} \qquad (1.4)$$

where R is the corrosion rate in mpy (mils penetration per year)

W is the weight loss in milligram

A is the area of the specimen in square inches

T is the time of exposure in hour

D is the density in g/cm^3

A variety of units have been used in the literature to express the corrosion rate. Corrosion rates are usually expressed in two basic unites mpy and mdd. (Milligram per square decimeter per day).

1.11 - Forms of Corrosion

a. General and local electrochemical corrosion [23]

When separate corrosion cells can be distinguished by variation of the electrode potential over the metal surface, by the appearance of corrosion currents or of separate anodic and cathodic corrosion products, local electrochemical corrosion is said to occur. General electrochemical corrosion occurs when separate anodic surfaces do not appear or they are of small dimensions (sub micro cells) or fluctuate over the surfaces to form a continuous film and retard continuous attack. Therefore general electrochemical corrosion leads to uniform attack whereas local electrochemical corrosion results in localized attacks.

b. Galvanic corrosion or dissimilar metal corrosion

Galvanic corrosion occurs when two or more dissimilar metals in electrical contact are placed in an electrolyte. This causes a potential difference between the metals which results in the flow of current between them. Several investigators [24, 25] have shown that galvanic corrosion is directly proportional to the area ratio of the cathodic metal to the anodic metal. Galvanic corrosion is maximum at the junction of the two metals. The attack decrease with increasing distance from the junction.

c. Crevice corrosion [26, 27]

This occurs in certain metal- environment combinations. Only metals and alloys which depend upon the oxide film for corrosion resistance are susceptible to crevice corrosion. It is an intense localized corrosive attack which occurs within the confined space or crevices created by certain mechanical configurations. They are created by surface deposits of corrosion products, scratches in paint film etc...

d. Filiform corrosion [28]

This is a special type of crevice corrosion which results in irregularly developed hair- fine lines or filaments of corrosion products below coatings of paints, tin, silver, etc. it does not destroy the component but affects the surface appearance.

e. Intergranular corrosion [29]

Grain boundaries are usually more reactive than the grain matrix. Hence localized attack occurs at adjacent to grain boundaries with relatively little corrosion of the matrix. This attack is usually rapid and penetrates deep into the metal resulting in loss of strength and causes catastrophic failures. Most metal alloys are susceptible to intergranular corrosion, when exposed to specific corrodents. Mostly corrosion of iron-nickel-chromium alloy is considered because of its commercial importance. Many reviews [30, 31] have appeared on this subject.

f. Pitting corrosion

This is also a form of intensive localized attack. The rate of attack being non-uniform. It is most destructive form of corrosion and results in sudden failure of the equipment due to the formation of pits or holes. It is reported to occur in the presence of chloride ions dependence upon the concentration of chloride ions [32- 35].

g. Exfoliation [36]

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

h. Stress corrosion cracking [37, 38]

The Cracking of metal or alloy due to the simultaneous presence of tensile stress and a specific corrosive environment is known as stress corrosion cracking.

i. Corrosion fatigue cracking [39, 40]

Reduction in the fatigue strength due to the presence of a corrosive environment is known as corrosion fatigue cracking. It occurs due to the combined action of cyclic stress and corrosive environment.

j. Fretting corrosion [41]

This type of corrosion occurs between two surfaces in contact with each other in dry or humid air when subjected to slight relative motion of small amplitude. Various alternate terms such as friction oxidation. Wear oxidation, chafing. False brinelling are used to describe these phenomena.

k. Erosion corrosion

Erosion corrosion is defined as increased corrosion rate to relative motion between metal surface and the environments usually liquid or gas. This type of corrosion is also known as impingement corrosion [36]. Such corrosion occurs in agitators, copper pipes, centrifuge etc. localized attack due to erosion corrosion usually has bright surface free from corrosion products e.g. Pits, grooves, rounded holes and valleys.

L-Cavitation corrosion [42]

This is a special type of erosion corrosion caused due to the formation of vapor bubbles in a corrosive environment near a metal surface and when the bubbles collapse attack arises. e.g. hydraulic turbulence, ship properties etc.

1.12- Methods of Preventing Corrosion [43]:

1. Methods based on modification of procedure:
   - (a) By attention to design.
   - (b) By application of cathodic protection.
2. Methods based on modification of the environment:
   - (a) By de-aeration or adjusting the pH of the environment.
   - (b) By purification or de- humidification of air.
   - (c) By addition of corrosion inhibitors.

3. Methods based on modification of the metal:
    - (a) By addition of alloying element.
    - (b) By heat treatment.

4. Methods based on protective coatings:
    - (a) Coating by reaction product (chemical or electrochemical treating of metal surfaces).
    - (b) Organic coatings (paint, resins, etc.).
    - (c) Inorganic coatings (enamels, cements).
    - (d) Metal coatings.
    - (e) Temporary protective.

1.13- Adsorption Isotherms

An adsorption isotherm is the mathematical expression which relates the bulk concentration of an adsorbing species to its surface concentration at constant temperature. An adsorption isotherm gives the relationship between the coverage of an interface with an adsorbed species (the amount adsorbed) and the concentration of the species in solution. Various adsorption isotherms have been formulated. A list of various isotherms and the corresponding equations are given in the Table (1.1) **[44]**. A common procedure is to convert isotherm to a linear form and plot the experimental data accordingly. The data can be fitted to any one of the adsorption isotherms from the suitable plot and the free energy of adsorption of the organic inhibitors can be obtained.

Most of the organic inhibitors obey Langmuir's or Temkin's adsorption isotherms. An inhibitor is found to obey Langmuir's isotherm if a plot of (log $\theta/1-\theta$) vs. (log C) is linear. Similarly for Temkin's plot of (θ) vs. (log C), for Bockris Devanathan and Muller (BDM) a plot of (log C – log $\theta/1-\theta$) vs. ($\theta^{3/2}$) and for the Frumkin's a plot of (log $\theta/(1-\theta)$ C) Vs (θ) will be linear.

Table (1.1). Adsorption isotherm

No.	Isotherm	Equations
1	Langmuir	$\beta C = \frac{\theta}{(1-\theta)}$
2	Freundlisch	$\beta C = \theta(\theta < n < 1)$
3	Frumkin	$\beta C = \frac{\theta}{(1-\theta)} \exp(-2a\theta)$
4	Temkin	$\beta C = \frac{\exp(a\theta) - 1}{1 - \exp[-a(1-\theta)]}$
5	Parsons	$\beta C = \frac{\theta}{(1-\theta)} \exp \frac{2-\theta}{(1-\theta)^2} \exp[-2a\theta]$
6	Bockris, Devanathan and Muller (BDM)	$\log C \pm \log \frac{\theta}{(1-\theta)} = C + \beta\theta^{3/2}$

Note: $\beta = e^{-\Delta G_{ads/RT}}$
a = interaction Parameter
a > o = attraction
a < o = repulsion

1.14-Literature Survey on the Corrosion Inhibition of Iron

The inhibition efficiency of the antibacterial cephalosporin (Cefotaxime, cefalexin, cefradine and cefazolin) for the corrosion of iron in 0.5 M H_2SO_4 and 1 M HCl was investigated using electrochemical techniques. The results of these techniques indicated that the inhibition efficiency increased with the concentration of inhibitor but decreased with temperature. Potentiodynamic studies proved that the inhibitors act as mixed mode of inhibition and the inhibitor molecules adsorb on the metal-solution interface. The adsorption of the inhibitors on iron surface obeys Langmuir adsorption isotherm equation.

All impedance spectra in EIS tests exhibit one capacitive loop which indicates that the corrosion reaction is controlled by charge transfer process. Inhibition efficiencies obtained from Tafel polarization, charge transfer resistance (R_{ct}) is consistent. One of the most important considerations in any industry is the reduction in overall cost in protection and maintenance of materials used. Because iron is the back bone of industrial consideration, the inhibition of the iron corrosion in acid solutions of organic inhibitors has been studied in considerable detail. Acids are widely used in many industries. Some of the important areas of application are industrial acid cleaning, pickling, decaling and in acidization of oil wells [45] It is reported that sulphur containing inhibitors such as sulphoxides [46, 47], sulphides[48], and thioureas[49] are found to be efficient in H_2SO_4 environment. 4-acetyl pyridine [50] aliphatic amines [51] substituted pyridine [52] aniline and alkyl aniline [53] p-substituted anilines [54] and n-substituted anilines [55] ortho-subistituted anilines [56] polyanilines [57, 58] and some heterocyclic compounds containing azole nucleus [59-64] inhibit the corrosion of steel in acid solution [65,66] have studied the effect of addition of triazole and their derivatives on the corrosion of mild steel in 1 M HCl and 0.5 M H_2SO_4 [67] have studied the effect of 2-(acetoacetamido) pyridine aryl hydrazone derivatives on the corrosion of iron in 0.5 N HNO_3.

These investigated inhibitors are classified as the first generation of cephalosporin and were found to have good activity against gram-positive bacteria and relatively moderate activity against gram-negative microorganisms [68]. No data are recorded in the literature about the behavior of this investigated cephalosporin as inhibitors for metallic corrosion. Most of the data recorded in the literature were about the electro analytical behavior of this investigated cephalosporin. These inhibitors were selected as inhibitors because: They are nontoxic, relatively cheap, and easy to produce in purities with proportion of more than 99 % and they are rich in donating atoms such as -N, -O and –S atoms.

Continuation to our goal for searching for safe, ecofriendly and non-toxic corrosion inhibitors, this work aims to investigate the inhibitive action of cephalosporin (which is a safe compound) towards the corrosion of iron in different acid solutions, namely HCl and H_2SO_4 using potentiodynamic and electrochemical impedance spectroscopy (EIS) techniques.

Corrosion inhibition using different inhibitors and the various factors affecting it were studied by many authors [69] .In the following a concise literature survey on the metallic corrosion and its inhibition by some related organic compounds in acidic medium.

Emregül and Orhan Atakol [70] studied the efficiency of N-(2-hydroxyphenyl) salicyaldimine [71], N,N bis-(salicyaldehyde)-1,3-diaminopropane[72] and N,N bis-(2-hydroxy benzyl)-1,3-diaminopropane[73],derived from the reduction of N,N- bis-(salicyaldehyde)-1,3-diaminopropane[72] ,as corrosion inhibitors has been studied weight loss , polarization and electrochemical impedance spectroscopy experiments have shown the reduced compound to be the best amongst the compounds studied [73].

Vraccar and Drazzicc[74] studied Adsorption and corrosion inhibitive properties of three different organic molecules:

2 - naphthalenesulfonic acid, 2,7-naphthalenedisulfonic acid and 2-naphthol-3,6- disulfonic acid are investigated on Armco-iron electrode cathodically polarized, in 0.5 mol dm^{3-} H_2SO_4 solution. The examinations show that the three organic molecules behave as cathodic corrosion inhibitors.

The inhibitive efficiency, changes with the number of functional groups substituted on benzene ring and increases with concentration. The experimentally obtained adsorption isotherms follow the Frumkin equation

$$[\Theta/n\,(1-\Theta)^{n}]\ \exp(-2a\Theta) = \beta_c$$

and the best fit is obtained for n = 2 (for 2-NSA) and n = 3 (for 2,7- NDSA and 2N-3, 6-DSA). The calculated values for the parameter a are 2.1–2.9 and Gibbs energies are 17–21 kJ mol^{-1}. The adsorption rate constants are very small, proving that iron surface permanently changes due to the corrosion processes.

Jeyaprabha *et al*[75] studied polymer amines such as polyaniline have been reported as an efficient corrosion inhibitor for iron in acid media. The performance of poly (diphenylamine) as corrosion inhibitor for iron in 0.5 M H_2SO_4 has been evaluated by potentiodynamic polarization, linear polarization and electrochemical impedance spectroscopy and compared with the performance of the diphenylamine monomer. It has been found that poly (diphenylamine) is an efficient inhibitor since the maximum efficiency of 96% has been observed at very low concentration of 10 ppm where as the monomer has given an efficiency of 75% at 1000 ppm. Besides, poly (diphenylamine) has been found to improve the passivation characteristics of iron in 0.5 M H_2SO_4. FTIR studies have shown that the poly (diphenylamine) is strongly adsorbed on the iron surface and inhibits the corrosion effectively.

Chetouani *et al*[76] studied inhibition by some newly synthesized pyridazine compounds of corrosion of pure iron in 1M HCl solution has been studied using weight loss measurements, polarization and impedance spectroscopy methods. The inhibiting action is more pronounced with stet-5-benzyl-6-methyl pyridazin-3-yl thioethanoic (P1) and (5-benzyl-6-

methylpyridazin-3-yl) ethyl thioethanoate (P3) and their inhibition efficiency increases with concentration to attain the of 85% and81% at the 10^{4-} M, respectively. We note good agreement between gravimetric and electrochemical methods (potentiodynamic polarization and maximum value impedance spectroscopy (EIS).

Polarization measurements show also that the pyridazines act essentially as cathodic inhibitors. The cathodic curves indicate that the reduction of proton at the pure iron surface happens with an activating mechanism. The presence of the sulphur atom increases the inhibition efficiency changing the adsorption mechanism.

Jeyaprabha *et al* studied **[77]**the inhibition of corrosion of pure iron in 0.5 M H_2SO_4 by ethanolamines such as mono-, di- and triethanolamines has been investigated by dc polarization and ac impedance techniques. The results showed that a strong dependence of inhibitor performance with concentration in addition to the structural effects of amine molecules. From impedance data it is found that the corrosion of iron is controlled by charge transfer process at all concentrations of inhibitors. All the three inhibitors are found to hinder the formation of passive film on iron.

Khaled and Hackerman studied **[78]** the inhibiting action of six o-substituted anilines against the corrosion of iron (99.9%) in solutions of sulphuric acid has been studied using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). At inhibitor concentration range (10^{-3} to 10^{-2} M) in 0.5 M acid, the efficiency of the inhibitors increases in the order o-toluidine < 2- chloroaniline < 2-ethylaniline < 2-fluoroaniline < o-aminoanisole < 2-amiophenetole.

Comparable results were obtained by the different electrochemical methods used. Adsorption of these compounds on the iron surface was found to obey a Langmuir adsorption isotherm. An equivalent circuit is suggested based on analysis of EIS data.

Sathiyanarayanan *et al*[79] studied Corrosion inhibitors are widely used in acid solutions during pickling and descaling. Mostly organic compounds containing N, O, and S groups are employed as inhibitors. The inhibition performance of metal cations such as Zn^{2+}, Mn^{2+} and Ce^{4+} ions in the concentration range 1-10 x 10^{-3} M has been found out. The corrosion behaviour of iron in 0.5 M H_2SO_4 in the presence of metal cations is studied using polarization and impedance methods. It is found that the addition of these metal cations inhibits the corrosion markedly. The inhibition effect is in the following order $Ce^{+4} >> Mn^{+2} > Zn^{+2}$.

El Achouri *et al* [80] studied three new gemini surfactants in the series of alkanediyl-α, ω-bis-(dimethylalkyl ammonium bromide) were synthesized and tested as corrosion inhibitors of iron in hydrochloric acid medium using gravimetric, electrochemical polarization and electrochemical impedance spectroscopy (EIS) measurements. Results obtained show that the surfactants studied are good cathodic inhibitors and act on the cathodic hydrogen reaction without modifying its mechanism. EIS results show that the changes in the impedance parameters (R_T and C_{dl}) with concentration of surfactants studied is indicative of the adsorption of molecules of surfactant leading to the formation of a protective layer on the surface of iron.

The effect of the temperature on the iron corrosion in both 1 M HCl and 1 M HCl with addition of various concentrations of 1,2-ethane bis-(dimethyl tetradecyl ammonium bromide) in the range of temperature 20–60^{o}C was studied. The associated apparent activation corrosion energy has been determined.

Chetouani *et al* [81] studied the inhibition of pure iron in 1 M HCl by new synthesized pyridazine compounds has been studied by weight loss, electrochemical polarization and electrochemical impedance spectroscopy (EIS) measurements. The results obtained reveal that these compounds are efficient inhibitors. The inhibition efficiency increases with the increase of inhibitor concentration and reached 98% at 10^{-4} M for 5-benzyl-6-methyl pyridazine-3-thione. Potentiodynamic polarization studies clearly reveal that the presence of pyridazines does not change the mechanism of hydrogen evolution and that they act essentially as cathodic inhibitors. The temperature effect on the corrosion behaviour of pure iron in 1 M HCl without and with the pyridazines at 10^{-4} M was studied in the temperature range from 298 to 353 K. EIS measurements show that the increase of the transfer resistance with the inhibitor concentration.

Khaled**[82]** studied the inhibitive action of some benzimidazole derivatives namely2- aminobenzimidazole (AB), 2-(2-pyridyl)benzimidazole (PB), 2-aminomethylbenzimidazole (MB), 2-hydroxybenzimidazole (HB) and benzimidazole (B), against the corrosion of iron (99.9%) in solutions of hydrochloric acid has been studied using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). At inhibitor concentration range (10^{-3}- 10^{-2} M) in 1 M acid, the results showed that these compounds suppressed both cathodic and anodic processes of iron corrosion in 1 M HCl by adsorption on the iron surface according to Langmuir adsorption isotherm. The efficiency of these inhibitors increases in the order AB> PB >MB >HB >B.

Both potentiodynamic and EIS measurements reveal that these compounds inhibit the iron corrosion in 1 M HCl and that the efficiency increases with increasing of the inhibitor concentration. Data obtained from EIS were analyzed to model the corrosion inhibition process through equivalent circuit. A correlation between the highest occupied molecular orbital E_{HOMO} and inhibition efficiencies was sought.

Jeyaprabha *et al***[83]** studied the synergistic effect of halide ions on the inhibition of corrosion of iron in 0.5 M H_2SO_4 solutions by polyaniline has been studied by polarization and impedance methods. Addition of 0.5×10^{-3} M I^- ions enhanced the inhibition efficiency of polyaniline at 10 ppm from 53% to 90%. However in the case of bromide and chloride ions, the inhibition efficiency of polyaniline at 50 ppm has been increased from 71% to 90%. The synergism parameter in all cases is found to be greater than 1. The synergistic effect is attributed to enhanced adsorption of polyaniline by the adsorbed halide ions.

Lgamri *et al*[84] studied the effect of a synthesized organic molecule containing heteroatoms such as nitrogen and sulphur on the corrosion behaviour of iron was investigated. Electrochemical studies of the iron samples were performed in an aerated solution of 1 M HCl by means of electrochemical impedance spectroscopy as well as polarization curves. The recorded electrochemical data showed that the corrosion resistance was greatly enhanced in presence of inhibitor; it acts at the same time on the anodic and cathodic electrochemical processes and its effect depends on its concentration. These results were confirmed by the impedance tests where it was observed that the effect of inhibitor addition appears by an increase in the resistance and especially by a strong reduction of the capacity of interface. Study of the temperature effect showed that the compound tested is adsorbed according to the model of Temkin. The maximal protection efficiency exceeded 94%. Theoretical calculations indicate that the protonation is easier on the site of the amine group. The corrosion protection could be explained by the adsorption of inhibitor through the N-atom and formation of a protective layer attached to the metal surface.

Chebabe *et al* [85] studied the efficiency of N-decyl, N-undecyl and N-dodecyl-1, 2, 4-triazole compounds as corrosion inhibitors of Armco iron, has been studied. Using weight loss and polarization data it has been shown that the N-dodecyl-1, 2, 4-triazole product was the best inhibitor, which acts on the hydrogen evolution reaction. Potentiodynamic polarization experiments showed that corrosion rate in presence and absence of N-dodecyl-1,2,4-triazole increases with increasing temperature from 30 to 60^{o} C.

The corresponding activation energies were determined. The high inhibition efficiency was obtained at 50^{o} C in presence of 10^{-3} M of N-dodecyl-

1, 2, 4-triazole. The effect of pH was examined from 0 to 3 values and the inhibiting effect decreases when pH value become higher than 2.

Shen *et al* [86] studied the corrosion behaviors of bulk nanocrystallized and coarse grain industrial pure iron (BNIPI & CGIPI) were investigated in 1 mol L^{-1} HCl at room temperature by means of electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curve. Mean while, the inhibitive effect of thiourea (TU) on the corrosion behaviors were tested. Results indicate that BNIPI is less prone to occur corrosion than its coarse grain counterpart in blank1 mol L^{-1} HCl at room temperature. When CGIPI was immersed for a very short time, namely, 5 min, an inductive loop appears at different concentrations at the Nyquist plots but it doesn't appear at those of BNIPI at the same period. A critical concentration of thiourea with the largest R_{ct} in the complex impedance plane appears for both samples.

Chetouani *et al*[87] studied inhibitory effect of some new synthesized tripyrazole compounds on corrosion of pure iron in 1 M HCl solution has been studied using weight-loss measurements and various electrochemical techniques polarization and impedance spectroscopy methods. The inhibiting action is more pronounced with *N*,*N*,*N*-tris[(3,5-dimethyl-1H-pyrazol-1-yl)methyl] amine (P1), and its inhibition efficiency increases with its concentration and attains the maximum value of 94% at the 2.5 x 10^{-4} M. The effect of temperature on the corrosion behaviour of iron was studied in the range from 298 to 353 K with and without P1 at 2.5 x 10^{-4} M. We note a good agreement between gravimetric and electrochemical methods potentiodynamic polarization and impedance spectroscopy (EIS). Polarization measurements show also that the compound acts mixed inhibitor. The catholic curves indicate that the reduction of proton at the pure iron surface happens within a pure activating mechanism. EIS measurements show the increase of the transfer resistance with the inhibitor concentration. The presence of the *N, N, N*-tris [(3, 5-dimethyl-1H-pyrazol-1-yl) methyl] amine increases the inhibition efficiency and not caused a drastic change in its adsorption mechanism. The adsorption of P1 on the surface of iron in 1 M HCl obeys a Langmuir isotherm adsorption.

Kertit *et al* **[88]** studied the mode of corrosion inhibition of pure iron due to l-phenyl-5- mercapto-1,2,3,4-tetrazole (PMT) in molar HCI is studied through weight loss and electrochemical steady-state experiments. From the comparison of results with those obtained using other “tetrazole’‘-type organic compounds, it is shown that PMT is the best inhibitor and its inhibition efficiency becomes 98% at 2 X 10^{-3}M. Polarization measurements show that PMT is a mixed-type inhibitor. PMT acts on the cathodic reaction without changing the mechanism of the hydrogen evolution reaction. The PMT appears to function through the general adsorption mode following the Langmuir adsorption isotherm model. The effect of temperature on iron corrosion behaviour in both 1M HCl and 1M HCl +10^{-3}M PMT have been studied. The inhibition efficiency of PMT is temperature-independent in the range 20-45^{o}C. The associated activation corrosion and adsorption energy has been determined.

Hongfang Ma *et al* **[89]** studied the self-assembled films of 1-methyl-5-mercapto-1, 2, 3, 4-tetrazole (MMT) were prepared on the iron surface. By means of electrochemical impedance spectroscopy in 0.5 M H_2SO_4 solutions, the inhibition ability of the film was investigated. Results were discussed through changing the concentrations of the inhibitor and the pH values of the self-assembly solutions. Quantum chemical calculation was applied to elucidate the adsorption mechanism of the inhibitor molecule to iron atom. The study shows that MMT is a good inhibitor for iron in 0.5 M H_2SO_4 solutions.

The self-assembled films formed in 10^{-2} M acidic solutions have the best protection effect and the inhibition efficiency in 0.5 M H_2SO_4 solutions is 98%.

Density functional theory proves that MMT molecule is adsorbed on the iron surface by the most negatively charged nitrogen atom and the adsorption can occur spontaneously.

AIM AND SCOPE OF THE PRESENT WORK

Iron has been extensively used under different conditions in petroleum industries [90]**.** Aqueous solutions of acids are among the most corrosive media. Acid solutions are widely used in industries for pickling, acid cleaning of boilers, decaling and oil well acidizing [91-95]. Mostly, sulfuric and hydrochloric acids are employed for such processes [92]. The main problem concerning iron applications is its relatively low corrosion resistance in acidic solutions. Several methods are currently used to prevent corrosion of iron. One of such methods in the use of organic inhibitors [91, 96, 97].

The present work was designed to:

1. Study the corrosion and corrosion inhibition of iron in HCl and H_2SO_4 solutions using green inhibitors.
2. Investigate the inhibiting effect of some ceohalosporins drugs as corrosion inhibitors for iron and determining the corrosion rate in the absence and presence of these ceohalosporins drugs by the electrochemical techniques (potentiodynamic polarization and ac impedance methods) at 298 and 303K.

This enables us to determine the:

(i) The activation thermodynamic parameters such as ΔH^*, ΔG^* and ΔS^*.

(ii) The type of adsorption isotherm and the kind of adsorption of inhibitors on metal surface (physical or chemical).

3. Study the effect of different substituted groups, whether electron donating or withdrawing, on the corrosion inhibition, the correlation between the type of the substituted group on the inhibition efficiency.

4. The surface examination using SEM and finally to rank the ceohalosporins drugs compounds according to their inhibition efficiency.
5. Calculate some quantum-chemical parameters and relate it to the inhibition efficiency.
6. Determine the mechanism and percentage inhibition of these ceohalosporins drugs.
7. Finally, ordered these ceohalosporins drugs according to their percentage inhibition.