# CHAPTER 1

# INTRODUCTION AND REVIEW

From the beginning of humankind itself, metals have been an inevitable part of human life. There are various forms of metals all over the world. Some of the metals exist in their pure form, whereas some of them exist as their ores. Gold is an example of native metal, whereas iron is seen as its ores in this world. When two or more metals are combined, it will convert into a more effective form, i.e. alloy. Steel is an alloy of iron (Fe) that has improved properties than Fe. The unique characteristics of steel are high strength, thermal stability and corrosion resistance. It causes wide applications of steel, especially in the construction fields. Based on the requirement of steel, different elements are added to it. Manganese, molybdenum, chromium, nickel, vanadium, silicon and boron are alloying elements.

Manufacturing technology and the cost of a material is an essential criterion for the selection of an alloy. It is tough to manufacture an alloy with the property of corrosion resistance cheaply. Mild steel is one of the readily available and easily manufactured alloys. It is a less carbon alloy. Other alloying elements are also present in a very negligible amount. So it is affordable steel to all. But, it undergoes oxidation (corrosion) readily if it is not protected by inhibitors, coatings, cathodic protection etc.[1]

## Corrosion

According to American Society for Testing and Materials' corrosion glossary, corrosion is defined as[2] "the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties". Corrosion is a metal destruction activity influencing the action of metal in applications badly. It is a natural process due to the presence of surrounding environments. When a pure metal is converted into its more stable metallic compounds (ores), it is known as corrosion[3]. The metallic compounds may be oxides, sulphides and carbonates. Rust is the corrosion product of ferrous metals. Adverse atmospheric conditions or aggressive media like acidic or basic solutions trigger corrosion in materials. All these natural deterioration processes cause acute damages to the surface of materials. Corrosion causes not only material loss but also economic loss. The financial loss due to corrosion is enormous all over the world every year. This loss can be divided into two cases 1) direct loss 2) indirect loss. Direct loss includes the cost of replacing and repairing corroded structures and machinery, galvanizing steel, modifying the metal by reforming it into alloy etc. Indirect loss can't be compensated by money, including the shutdown of industries, loss of products, and efficiency.

Each metal has different corrosion resistance power. The corrosion due to atmospheric exposure on steel, the most popular alloy, is uniform in nature. That is uniform corrosion. Localized corrosion is difficult to predict and reduce. Various type of corrosion exists in chemical industries due to the presence of offensive corrodents. According to DIN EN ISO 8044, corrosion[4] is the "physical interaction between a metal and its environment which results in changes of the properties of the metals and may lead to significant functional impairment of the metal, the environment or the technical system which they form a part".

## Mechanism of corrosion

### *Local cell theory*

According to De la Rive "corrosion occurs because of creating a large number of micro electrochemical cells or local cells at heterogeneities (impurities, defects, different phases, non-uniform stress distribution etc.,) on the metal surface[5]". This is the basics of Local cell theory of corrosion (Fig. 1.1). A change in electrical potential experienced between two metals or between various portions of a single metal during the corrosion process. This voltage difference develops the current to go through the metal accounts for the reaction at anodic and cathodic areas. The difference in composition on the metal surface, surface inhomogeneity and stress due to metal operational works cause the development of anodic and cathodic areas on the metal surface.

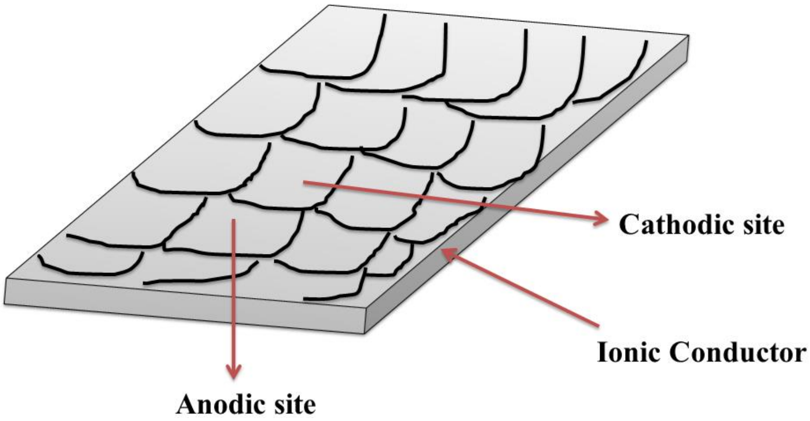


Fig. 1.1: Pictorial representation of local cell theory

***Wagner and Trauds' theory***

Primary mechanism of corrosion includes an occurrence of corrosion cells; however, it is not necessary to exist physically independent anodes and cathodes to take place corrosion. Instead of impurities and surface irregularities, some cathodic reactions must carry on concurrently on the metal surface. These cathodic reactions are the essential condition for corrosion as per Wagner and Trauds' theory[6].

Corrosion which is a metal dissolution process, can be explained using the following steps (Fig. 1.2):

- In the first step, $Fe^0$ getting oxidized into $Fe^{2+}$ ion. Here iron is lost from the cathodic site, the smaller potential site to the aqueous solution.
- When $Fe^{2+}$ formed, two electrons will be free to move through the metal surface to the cathodic site.
- Released electrons consume by oxygen in the water and converted into $OH^-$.

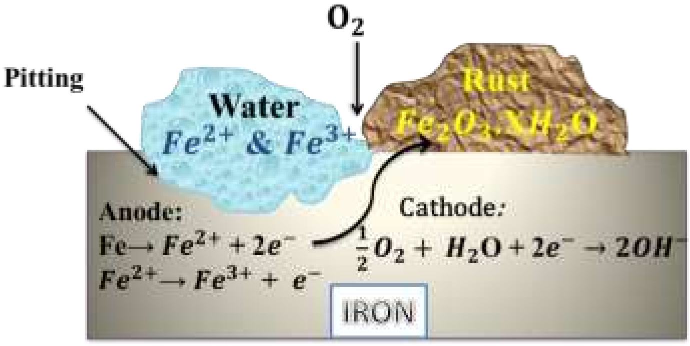


Fig. 1.2: Reactions involved in the corrosion of iron

Reaction at Anode: $Fe \rightarrow Fe^{2+} + 2e^{-}$ (1)

Reaction at Cathode: $\frac{1}{2}O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-}$ If $P^H > 4$ (2)

If oxygen is not present, $H^+$ controls the reaction at the cathode to maintain the electrical circuit.

$2H^{+} + 2e^{-} \rightarrow H_2\uparrow$ (3)

Hydroxyl ions react with $Fe^{2+}$ to form the less soluble ferrous hydroxide, precipitating a white loosely clumped mass of fine suspended particles at the metal surface.

$Fe^{2+} + 2OH^{-} \longrightarrow Fe(OH)_2\downarrow$ (4)

This powder easily reformed into ferric hydroxide by oxidation.

$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3$ (5)

Ferric hydroxide undergoes dehydration causes the occurrence of corrosion products on the metal surface.

$2Fe(OH)_3 \longrightarrow Fe_2O_3\downarrow + 3H_2O$ (6)

$Fe(OH)_3 \longrightarrow FeO(OH)\downarrow + H_2O$ (7)

It may lead to the precipitation of other aqueous ions since solid corrosion products are formed at the anodic site. It may attribute to the formation of traces of suspended mud, sand, clay etc., on the corrosion film. A porous film indicates that corrosion can occur continuously due to the penetration of metal ions up to the solution interface, whereas a tight adherent film shows the elimination of ionic diffusion.

## Types of corrosion

The most adapted classification of corrosion provides the study of corrosion in depth[7, 8]. Corrosion failure analysis requires the knowledge of types of corrosion which is responsible for deterioration.

### *Uniform corrosion*

It is also known as general corrosion[1]. It leads to the uniform thinning of corrosion over the metal surface. It is due to the existence of manifold anodes and cathodes working on metal surfaces like local corrosion cells. Uniform corrosion is made possible by the continuous movement of the anodic and cathodic sites over the surface. The impact of uniform corrosion can be easily judged because it is reproducible. Irrespective of the environment, the exposed metal surface is wholly corroded in this corrosion. The different environments are liquid electrolyte, gaseous electrolyte or hybrid electrolyte.

The anodic reaction of uniform corrosion is an oxidation process at all times. The cathodic reaction depends on the conditions: If $P^H < 7$ reduces hydrogen ions; If $P^H \geq 7$, it reduces dissolved oxygen. By applying paints, coatings or inhibitors, uniform corrosion can be prevented.

### *Galvanic corrosion*

It is called dissimilar metal corrosion or bimetallic corrosion. It is formed by joining two different metals to build a wet corrosion cell (Fig. 1.3). The requirement of galvanic corrosion is an electrolyte and an electron-conducting path. Galvanic series determines which metal is acting as anode and cathode in the cell. The more negative metal will be the anode, and the more positive metal will be the cathode of the corrosion cell. The corrosion rate of the more active anode will increase, and of nobler cathode will decreases. The junction between two metals acutely undergoes corrosion. The voltage difference between different metals leads to this corrosion. The conductivity of the electrolyte and the area ratio between cathode and anode are the two essential factors that determine the degree of attack. For example, galvanic corrosion results when aluminium alloy is coupled with steel and enhance the rate of corrosion of aluminium alloy which is the anode.

Fig. 1.3: Mild steel coupled with copper showing galvanic corrosion

***Crevice corrosion***

It is the same as pitting corrosion. In this corrosion, the total exposed area undergoes local changes in its chemistry. Reduction of oxygen in the crevice, increase in pH with increasing hydrogen ions and chloride ions are some of the initiations of crevice corrosion. Reduction of oxygen is a cathodic process that cannot exist under the crevice area causes metal dissolution.

Crevice corrosion may operate with any metal and adverse environment. However, certain metals and alloys specifically undergo crevice corrosion in particular environments because they depend on their oxide film at the surface of the material for the prevention of corrosion. Previous reports show that other than metallic material, wood, wax, plastic, rubber, concrete etc., are prone to crevice corrosion. It is generally exhibited in chloride environments.

### *Filiform corrosion*

It is a form of crevice corrosion, also called “under film” corrosion. By the exposure of atmospheric moisture on painted surfaces, filiform corrosion takes place. Lacquers painted surfaces are mainly affected by this corrosion. Therefore, such quick-dry paints should avoid the prevention of this type of corrosion.

### *Pitting corrosion*

Pitting corrosion is another form of crevice corrosion. It is self-nucleating localized corrosion. The attacking areas of pitting corrosion may include surface scratch or an emerging dislocation due to the applied tensile stresses or non-homogeneous composition (Fig. 1.4). Its initiation depends only on metallurgical factors.

Fig. 1.4: Pitting corrosion of mild steel

It is more harmful than uniform corrosion because it is not easy to detect and resist. Even a tiny pit can destruct the whole engineering system. After the initiation, the same cathodic reactions, such as oxygen depletion, hydrogen evolution etc., occurs in the pits as the crevice corrosion.  The pits will act as an anode and the remaining metal surface act as a cathode. So, the metal loss will take place in small pits and reach higher rates than general corrosion. Large pits are challenging to corrode due to the mixing and restoring of oxygen, hydrogen or bicarbonate ions by water mobility.

***Intergranular corrosion***

Intergranular corrosion is a form of localized corrosion. It is a selective attack on the grain boundary area near them. The strength and ductility of a metal reduce because there is no damage to the centre of the grain. The attack is random, piercing into the metal and causing deterioration.

***Stress corrosion cracking (SCC)***

Structural components of a system may collapse before the due time when they are forced to the tensile stress and aggressive environment (Fig. 1.5). This phenomenon is called environmentally induced cracking (EIC). EIC includes three different forms of corrosion.

- Stress-corrosion cracking (SCC)
- Hydrogen-induced cracking (HIC)
- Corrosion-fatigue cracking (CFC)

Fig. 1.5: Stress-corrosion cracking of mild steel

***Erosion corrosion***

The word “erosion” implies destruction via mechanical force such as wear and tear. When erosion facilitates the rate of corrosion of a metal, it is known as erosion-corrosion. The critical reasons for erosion-corrosion are corrosive environment and elevated fluid surface velocities. Unlike other corrosions, the surface of metal subjected to erosion-corrosion will be clear.

**Necessity of corrosion control**

For the years, the study of corrosion and its prevention methods have been gaining traction in the research world. This is due to:

- The utilization of a variety of metals and newly synthesized alloys has grown to a great extent.
- The need for metals in specific areas like aerospace, atomic energy etc. increasing in recent years.
- The increasing environmental pollution originates from aggressive corrosion conditions.
- Occasionally, the depletion of metal structures to thinner dimensions may be due to economic inducements; thus, the consequences of corrosion are extended to a necessary extent.
- The soaring trend toward prolonged time between support, swift restorative effort and the preference to track tasks involuntarily.
- The industry pays a heavy toll on corrosion. However, a considerable section of these costs could be conserved by an efficient implementation of well-known procedures for corrosion prevention paired with the growth of more effective approaches of protection[9].

Various nations reported in their studies that corrosion is a significant issue they face. The United States revealed that around 5% of the GDP was destroyed due to corrosion[3]. It has been considered that 20-25% of the current corrosion costs could be reserved by employing existing awareness of corrosion inhibition and control, i.e., applying recommended protective systems and upgrading design and materials selection[10, 11].

Beyond the economic loss of corrosion are safety matters. Human society focuses its attention on the security of a range of metallic structures susceptible to corrosion ruins. For example, aeroplanes constructed from extremely strong aluminium alloys and pressure vessels could threaten many lives if collapsed[12]. Besides all these, corrosion is severe destruction because it engenders the impoverishment of our natural resources. The enhancing industrial advancements of many countries cause an increased demand for metal resources to become more inadequate. It should also be suggested that the prevention of corrosion conserve energy[13]. In the concept that the extraction of all metals from their ores depleting vast amounts of energy. Preserving metals in their original state thus deliver a large quantity of energy. The applicability of corrosion to the community lies in the extensive use of metals exposed to various challenging environments[14].

## Methods for corrosion control

The relevant stages of a component during its lifespan are design, construction and application. Corrosion inhibition has a vital role in each of these stages. Therefore, the breakdown of corrosion control in any of these stages will damage the component untimely.

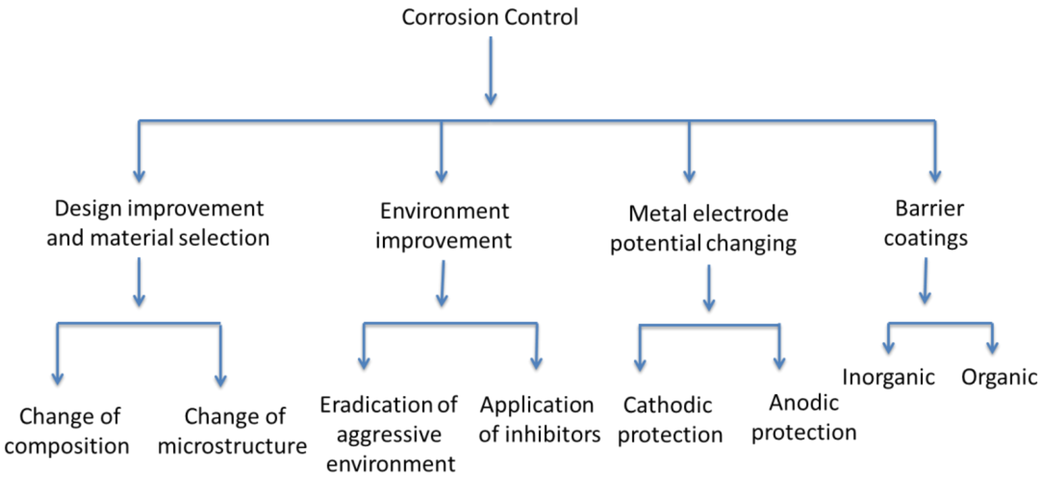


Fig. 1.6: Schematic representation of corrosion control methods

Corrosion control can be done by

- Improving the design and material selection
- Improving the environment
- Implementing barrier coats
- Implementing cathodic or anodic protection.

***Materials selection and design***

A proper design includes both mechanical and strength requirements, which means it allows free circulation of air instead of the build-up of dirt and stagnation of water. The selection of suitable material and its design is the initial step for corrosion control. For example, the relevance of metallurgical phase composition can be exemplified by the exfoliation of aluminium in marine life.

***Improving the environment***

There are two strategies for electrolyte management:

❖ ***Eradication of the aggressive components***

The following methods explain the removal of aggressive components:

1) Addition of oxygen scavengers, saturation of inert gases like $N_2$, evacuation etc., causes the removal of dissolved oxygen from the solution.
2) Neutralization reactions can remove corrosive acids or bases.
3) Prevention of humidity by any drying agents like silica gel.
4) Ion exchange or reverse osmosis can eradicate dissolved salts from the solution.
5) Relative humidity can also reduce by increasing the temperature above the surroundings.
6) Removal of solid particles causes the prevention of different aerations and crevice erosion.

## ❖ *Application of inhibitors*

The use of corrosion inhibitors is an efficient and reliable method for shielding metals from deterioration in contact with aqueous solutions, especially in a closed system like cooling and heating systems[15]. Corrosion inhibitors are organic or inorganic compounds, which retard the rate of corrosion when added to the solution in a low concentration ranging from 1 to 15,000 ppm.  Two probable working methods are for corrosion inhibitors to control metal corrosion in a corrosive environment[16]. 1) By the interaction with the corrosive species 2) By the interaction with the metal surface

Adsorption is the chief phenomenon through which corrosion mitigation happens on the metal surface by decreasing the rate of either or both the anodic and cathodic reactions. Inhibitors have a pronounced effect on the $H_2$ evolution reaction, such as aromatic and aliphatic amines; phosphorous, arsenic and antimony compounds; sulphur compounds and carbonyl molecules in the metal dissolution process. Some of the inhibitors create shielding to the metal surface by precipitating on it. Phosphate and bicarbonate salts of multivalent ions can form a passivation layer since they are insoluble. Another class of inhibitors works as redox agents by cathodic or anodic protection. Chromate is an example of a redox inhibitor that alters the potential of a metal surface and develops a passivation layer. Depending on the mechanism of inhibition, corrosion inhibitors are categorized into anodic, cathodic, mixed type and vapour phase inhibitors.

### *Anodic inhibitors*

They are passivating inhibitors that inhibit metal corrosion by developing a barrier of oxide film on the metal surface. They affect the rate of anodic reactions in the corrosion process. There are two types of passivation by inhibitors 1) oxidizing 2) non-oxidizing. Nitrite, chromate, nitrate etc., passivate metal without oxygen. They belong to oxidizing inhibitors. Some of the inhibitors like tungstate, molybdate, phosphate etc., passivate metal with oxygen. They are called non-oxidizing inhibitors. The important condition for an anodic inhibitor is that its concentration must be high in solution. Otherwise, it causes localized corrosion on the metal surface because the inhibitor doesn’t adsorb the surface entirely.

*Cathodic inhibitors*

They affect the cathodic reaction and control the migration of ions to the cathodic site[17]. They can perform in different ways, such as cathodic poisons, cathodic precipitates and oxygen scavengers. Sulphites, bicarbonates etc., belong to cathodic inhibitors[18]. They are more advantageous than anodic inhibitors since cathodic inhibitors demand only a small amount of inhibitors.

*Mixed-type inhibitors*

They control both anodic and cathodic reactions of a corrosion process. The organic inhibitors usually act as mixed-type inhibitors by resisting metal dissolution at the anode and oxygen reduction at the cathode.

*Vapour phase inhibitors (VPIs)*

They have low vapour pressures ranging from 0.0002 to 0.4 mmHg. They can volatilize easily and adsorb on all surfaces situated in a confined space[19]. Their lifetime is so vast. So, they can retard the corrosion of metals used in storage, transport and electronic materials, such as circuit boards. VPIs are commonly used for the protection of steel. Hydrazine and morpholine are good examples of vapour phase inhibitors. They are carried with steam to prevent corrosion in condenser tubes.

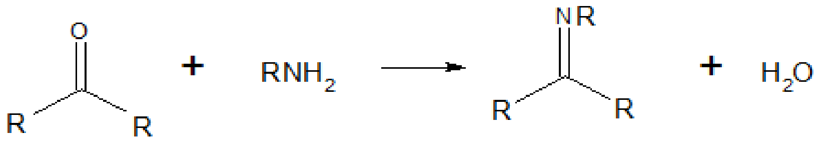
Corrosion inhibitors are further classified into two based on compounds, i.e., organic and inorganic inhibitors.

*Inorganic inhibitors*

Molybdate anion, calcium nitrite, zinc phosphate, chromate, rare earth metal salts etc., belong to this category[20]. However, their application as an inhibitor is less due to its high toxicity, high cost and less solubility.

*Organic inhibitors*

Low toxicity, high solubility, coexistence with the protected metal and withstandable at various temperatures make them most popular in industrial fields. They form a protective film on the metal surface by performing either anodic, cathodic or mixed inhibitors. Plant extracts, amines, amino acids, heterocyclic compounds and Schiff bases are few examples of organic inhibitors in which Schiff bases are commonly used synthetic organic inhibitors. Condensation of an amino compound with aldehyde or ketone produces a Schiff base with a general formula $R_2C=NR$. It has been reported that Schiff bases have good corrosion inhibition capacity than their parent compounds. –CH=N- group involved in Schiff bases causes physical and chemical adsorption on the metal surface. Adsorption mainly depends on three factors. 1) structure of the inhibitor, 2) characteristics of the metal surface and 3) corrosive medium. Only the molecules having heteroatoms such as N, O and S and conjugated unsaturated π bonds can create adsorption film on the metal surface by donating lone pair of electrons and π electrons respectively[21,22].



### ❖ ***Application of barrier coats***

A variety of barrier coatings may be employed to minimize localized corrosion on the metal surface. Barrier coatings protect the metal by high resistance to inhibit current flow between anode and cathode or dispossess oxygen diffusion. Metallic, inorganic and organic coatings are different materials for protection. Thin coatings of materials can protect the metal from its environment with an acceptable barrier. Based on the service condition and economics for a certain process, the applicability of the barrier coating varies.

- ***Shifting the electrode potential***

According to the principle of anodic protection, a metal can protect either cathodically by decreasing its potential to the region of immunity or increasing the potential to the region of passivity. In the case of iron, elevation in the potential can be achieved by anodic polarisation or the addition of appropriate oxidizing agents. Metal protection by raising the potential is an excellent corrosion control method for iron-based metals and alloys in acid solutions since the region of passivity for iron is notably larger, as shown in Pourbaix diagram[23] (Fig. 1.7).

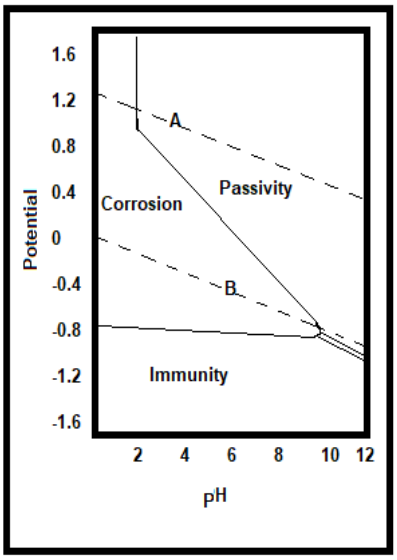


Fig. 1.7: Pourbaix diagram for iron in aqueous solution

Cathodic protection can be employed by sacrificial anodes or impressed current[24]. An electrolysis cell is built in the sacrificial method by connecting the metal to be protected with a more quickly destructed sacrificial metal intentionally. A sacrificial anode is set up from a metal having more negative potential than the metal to be protected, which furnishes adequately high protective current. The potential difference between the sacrificial metal and the metal to be protected means the sacrificial metal deteriorates in preference to the metal to be protected. There are two necessary conditions for working the sacrificial anode method 1) for the flow of electrons from the sacrificial anode to the metal to be protected; a current path should be set up 2) There should be an electrolyte to carry the electrons. This method requires no external power source, whereas the impressed current method employs a power source to supply electrical power to the metal to be protected by the aid of an auxiliary electrode. Therefore, the impressed current method provides much longer protection than the sacrificial anode method since the former is connected by an outside power source[25].

### Corrosion monitoring techniques

Corrosion analysis involves a quantitative measurement of the efficacy of corrosion regulation and evaluation of inhibition techniques. The significant advantages of corrosion monitoring may be summarized as[9].

- Better safety
- More eco-friendly
- A continuous and dynamic record of metal stability
- Lower performance costs

#### ***Weight loss measurements***

One of the oldest direct measurement techniques of corrosion is the weight loss method, which employs metal weight loss over a coupon strip. The easiness of detection of small weight losses depends on the ratio between surface area and coupon weight. This prefers the shortest interval of time between weighing instead of a long time gap which will cause loss of rate of attack fluctuations. But, in the case of large samples, a long time interval of weighing is desired to monitor pitting attacks.

This method requires the weight loss of a metal exposed in the acid medium with and without inhibitor at a particular time interval in corrosion studies. Using the resulted weight loss values, corrosion rate ($\upsilon$) and inhibition efficiencies ($\eta\%$) are estimated by the following equations.

$$\upsilon = \frac{KW}{DSt} \tag{8}$$

where K =87600, W- an average weight loss of coupon (g), S- total area of the coupon ($cm^2$), D- density of metal ($g\ cm^{-3}$), t- period of immersion (h).

$$\eta\% = \frac{\upsilon_0 - \upsilon}{\upsilon_0} X100 \tag{9}$$

where $\upsilon_0$ and $\upsilon$ indicate the corrosion rate of metal coupons immersed in acid solutions in the absence and presence of the inhibitor.

### *Electrochemical impedance spectroscopy (EIS)*

Electrochemical impedance spectroscopy is the plot of electrode impedance against frequency. Dynamics of an electrochemical process is described graphically in EIS. It is an alternate current method that provides equivalent resistance and capacitance values in terms of interfacial phenomena.

A sinusoidal voltage perturbation of low amplitude is applied in the electrochemical system for EIS in a boundary of frequency. Frequency is the unique character of various processes involved in the electrochemical system since the processes evolved are distinct at each frequency. For an excitation signal $\omega$, a linear system outputs a current frequency $\omega$ whereas; a non-linear system outputs a current with contorted frequency. The effect of non-linearity can be detected and applied for an electrode reaction in which the current-over potential function is non-linear beyond average ranges of overpotential. The flexibility of charging currents is the best part of all methods based on non-linearity. Charging currents are highly regulated to the excitation signals because double-layer capacitance has a more linear effect than faradaic impedance.

Corrosion behaviour can be analyzed using EIS at the metal/solution interface. In the corrosion process, the measured current is out of phase with the input voltage. Impedance is the fraction of input voltage to the output current. The fluctuation in magnitude and phase angle of impedance value gives elucidation of EIS. Electrical equivalent circuits are characteristic of the electrochemical reactions at the interface between metal and electrolyte. So, all the analysis of impedance data is focused on it.

Equivalent circuit of a cell is identical to the system in an electrochemical cell. The working of an electrochemical cell can render by an equivalent circuit of resistors and capacitors. As the real cell performs for a given signal, the equivalent circuit convey the current with the same amplitude and phase angle. Randle’s circuit is the most commonly employed equivalent circuit. It consists of a solution resistance, a double layer capacitance ($C_{dl}$) and a charge transfer resistance ($R_{ct}$) or polarization resistance ($R_p$). Charge transfer reaction in the electrochemical cell makes the double layer capacitance parallel with the impedance[26]. Generally, double-layer capacitance on real cells acts as a capacitor. Fig. 1.8 represents Randle’s circuit.

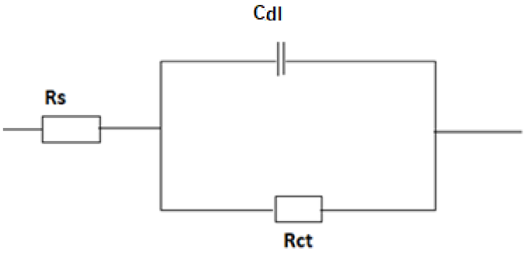


Fig. 1.8: Randle’s circuit

This is the case of ideally behaving capacitors. Actually, capacitors perform as a constant phase element in the electrochemical system.  This is because of the conjoining of the solution resistance and the surface capacitance due to microscopic roughness on the metal surface by corrosion attack, damage etc. Moreover, chemical in-homogeneities of the surface also lead to capacitance dispersion at the interface. These two factors cause the non-ideal behaviour of capacitors.

A sinusoidal voltage may be represented as

$$e = E\mathrm{Sin}\omega t \tag{10}$$

where $\omega$ is the angular frequency.

Phase angle between I and E will be $\emptyset$ in real cases. So, it may be expressed as

$$i = I\mathrm{Sin}(\omega t + \emptyset) \tag{11}$$

where $\emptyset$ is negative.

These equations may be utilized for the evaluation of simple circuits. When a pure resistance R is applied to this sinusoidal voltage, the current will be

$$i = ({}^{E}/_{R})\mathrm{Sin}(\omega t + \emptyset) \tag{12}$$

where $E = IR$ (13)

If $\emptyset$=0, then

$$i = ({}^{E}/_{R})\mathrm{Sin}\omega t \tag{14}$$

When a pure capacitor replaces the resistor, then current will be

$$i = \left({}^{E}/_{X_c}\right)\mathrm{Sin}(\omega t + {}^{\pi}/_{2}) \tag{15}$$

where the phase angle is ${}^{\pi}/_{2}$ and the current peaks come earlier than the voltage peaks. Real components are obtained along the abscissa, while imaginary components are availed along the ordinate. It is convenient to plot the current phase along the abscissa.

$$E = -jX_cI \tag{16}$$

where $j = \sqrt{-1}$ (17)

On comparing (13) and (16), it is clear that $X_c$ has the exact characteristics of resistance except for the correlation between its magnitude and frequency. The magnitude of $X_c$ is inversely proportional to frequency.

When resistance R and capacitance C are connected in series, a voltage E is applied. The sum of individual contributions of the resistor and capacitor is the total voltage drop.

$$\mathrm{E} = \mathrm{E_R} + \mathrm{E_C} \tag{18}$$

$$\mathrm{E} = \mathrm{I(R - jXc)} \tag{19}$$

$$\mathrm{E} = \mathrm{IZ} \tag{20}$$

This Z vector is known as an impedance that links between voltage and current. Impedance can be expressed as

$$\mathrm{Z_\omega} = \mathrm{Z_{Re}} - \mathrm{jZ_{Im}} \tag{21}$$

where $\mathrm{Z_{Re}}$ represents real components, and $\mathrm{Z_{Im}}$ indicates imaginary components of the impedance.

For the combination of resistors and capacitors, phase angles are between 0 and $\frac{\pi}{2}$. There are different forms of representations for recording fluctuations in impedance with frequency.

Bode and Nyquist plots are two other representations (Fig. 1.9). Bode plot[27] exhibits log $|\mathrm{Z}|$ and $\emptyset$ against log ω, whereas Nyquist plot represents $\mathrm{Z_{Re}}$ against $\mathrm{Z_{Im}}$ for various $\omega$.

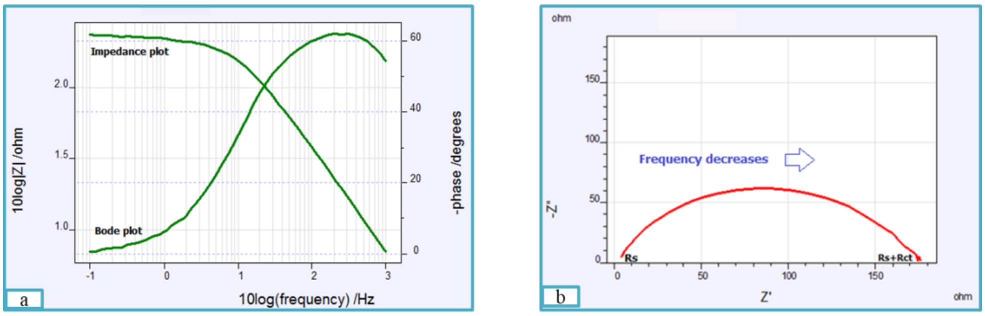


Fig. 1.9: a) Bode plot b) Nyquist plot

Bode plots precisely express frequency information. In the Bode plot, the same number of points is recorded for each decade. So, it is plotted over the observed frequency region logarithmically. To find the initial resistor more easily, both Nyquist and Bode plots depict high frequency to low frequency. Nyquist plot is a popular representation of impedance since it is more interpretative than the other. In the Nyquist plot, the real part is plotted against the imaginary part and gives impedance values for various frequencies. Impedance decreases as frequency increases.

To counteract solution resistance between the counter and reference electrodes, three-electrode assembly is used in electrochemical systems. But, when the electrochemical cell is designed, there is a solution resistance between the reference electrode and the working electrode that should be accounted for. Impedance is a degree of the capacity of an electrical circuit to resist the conveyance of current, similar to resistance. But, impedance doesn't follow the simplifying properties of an ideal resistor. An ideal resistor

a) Obeys Ohm's law at all current and voltage values.

b) Its resistance value doesn't depend on the frequency

c) Alternate current and voltage signals through a resistor are in phase with each other.

EIS is a dominant technique for the quick and precise analysis of corrosion processes of various materials in different corrosive media[28]. It is also used to delineate coating integrity. Organic coatings have high resistivity. So, typical DC techniques can't employ for the analysis of corrosion[29]. EIS technique provides necessary parameters for estimating corrosion mechanisms such as coating capacitance, coating resistance, and interfacial corrosion process between metal and coating[30].

Nyquist plot is a semi-circular line for Randle's equivalent circuit. Real axis value at the high-frequency intercept, close to the origin, gives the solution resistance. In contrast, charge transfer resistance (polarization resistance) and solution resistance at the low-frequency intercept gives total resistance. So, the measurement of the diameter of the semicircle provides charge transfer resistance. Other parameters obtained from the Nyquist plot are corrosion rate, corrosion current and capacitance of coating. Using $R_{ct}$ values from Nyquist plots, the corrosion inhibition efficiency of an inhibitor can be determined by the following equation.

$$\eta\,\% = \frac{R'_{ct} - R_{ct}}{R'_{ct}} X100 \tag{22}$$

where $R'_{ct}$ and $R_{ct}$ are the charge transfer resistance of the working electrode in the presence and absence of inhibitor, respectively.

***Potentiodynamic polarization method***

Polarization of an electrode results from dispelling the potential of an electrode from its original value at an open circuit. Polarisation leads to the conveyance of current at the electrode surface. This departure from the equilibrium condition leads to a potential difference between polarized and unpolarized electrode potential. That is referred to as overpotential ($\eta$)[31]. The degree of polarization can be obtained from the value of over potential $\eta$,

$$\eta = E - E_{eq} \tag{23}$$

Polarization related to the charge transfer mechanism is known as activation polarization. The following equation connects reaction rate and overvoltage for activation polarization,

$$\eta_a = \pm \beta \log \frac{i}{i_0} \tag{24}$$

where $\eta_a$ represents overvoltage, $\beta$ indicates a constant called Tafel constant or “$\beta$ slope[30]”, and i is the current density which explains the rate of oxidation or reduction. This equation is known as the Tafel equation.

Reaction rate in a corrosion process is equivalent to electric current due to the movement of electrons and ions from metal to solution and vice-versa. Potential of the metal also determine the reaction rate. If the potential of metal is more positive, then there is an increase in anodic reaction rate and a decrease in cathodic reaction rate. If the potential of metal is more negative, then the opposite phenomenon takes place on the reaction rate. So, the corrosion process can be monitored using current-potential curves. Polarization curves are current-potential curves under certain polarization conditions. Fig. 1.10a and b show the Tafel plot and linear polarization curve, respectively.

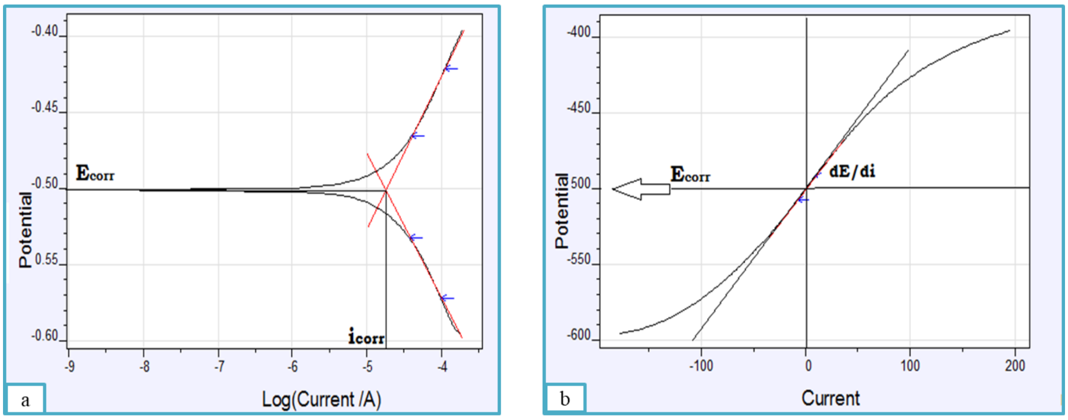


Fig. 1.10 a) Tafel plot b) Linear polarization curve

❖ ***Tafel extrapolation method***

It depends on the mixed potential theory discovered by Wagner and Traud[32]. Information availed from cathodic or anodic polarization measurements are applied in this method. The mixed potential at which anodic and cathodic reaction rates are equal is called open circuit potential (OCP)[33], or corrosion potential $E_{corr}$ and corresponding current is called corrosion current density $i_{corr}$. Initially, the voltmeter records the corrosion potential of the metal concerning the reference electrode before the conveyance of cathodic current. After cathodic polarization, by applying external potential E ($E_{corr}$>>E), the applied or measured current density can be expressed similarly to the Butler-Volmer equation[34],

$$i_{app} = i_{corr}\{\exp[-\frac{\alpha_c}{RT} zF\eta]\} \quad (25)$$

where $\eta = E - E_{corr}$ , (26)

$\alpha_c$ represents the charge transfer coefficients for cathodic reactions, $\eta$ is the overpotential, z is the valency of metal, T is the absolute temperature, F and R represent Faraday constant and universal gas constant, respectively.

Tafel slope for cathodic polarization is given by,

$$b_c = \frac{2.303\ RT}{\alpha_c\ zF} \quad (27)$$

If anodic polarization takes place by applying $E >> E_{corr}$, the expression for the applied or measured current density is,

$$i_{app} = i_{corr}\{\exp\left[\frac{\alpha_a}{RT} zF\eta\right]\} \quad (28)$$

where $\alpha_a$ represents the charge transfer coefficients for anodic reactions.

Tafel slope for anodic polarization can be expressed as,

$$b_a = \frac{2.303\ RT}{\alpha_a\ zF} \quad (29)$$

Corrosion current density is different for inhibited and uninhibited corrosive media. Its value is lower in the inhibited medium since the inhibitor decreases the rate of the corrosion process. So, percentage inhibition efficiency can be calculated as,

$$\eta_{pol}\% = \frac{i_{corr} - i'_{corr}}{i_{corr}} X100 \quad (30)$$

where $i_{corr}$ and $i'_{corr}$ are the corrosion current densities in the absence and presence of the inhibitor.

Values of $b_a$ and $b_c$ help to determine the mechanism of inhibitor. If there is a large deviation only in $b_a$ values of the inhibited media from the uninhibited one, it can be said that there is remarkable adsorption of inhibitor molecules on anodic site only. Similarly, the deviations in $b_c$ value correspond to the influence of inhibitor molecules on the cathodic site only. On the other hand, if both $b_a$ and $b_c$ values considerably change, it causes adsorption of inhibitor molecules on both anodic and cathodic sites, affecting both anodic and cathodic corrosion.

- ***Linear polarization method***

When anodic and cathodic reaction rates are equal, the potential acquired for the metal in corrosive solution is known as corrosion potential. After repositioning the corrosion potential $E_{corr}$ of the metal, there will be a polarization resistance $R_p$ which is the slope of the linear polarization curve dE/di. As the polarization resistance increases, corrosion current density $i_{corr}$ lowers and thereby, corrosion rate also decreases. The relationship between $i_{corr}$ and $R_p$ is shown in the following equation[35].

$$\mathrm{i_{corr}} = \frac{\mathrm{B}}{\mathrm{R_p}} \tag{31}$$

where B is a constant.

Polarization curves progressively diverge from the linear relationship on the logarithm of current density after the polarization of the metal is raised over 10 mV. In such cases, the measured potential E and current density 'i' relates to the following equation.

$$\mathrm{E} - \eta = \mathrm{i_0} + \mathrm{blogi} \tag{32}$$

where $\eta$ indicates the overpotential, $\mathrm{i_0}$ represents the exchange current density, and b gives the Tafel slope dE/dlogi of the curve.

Polarization resistance $R_p$ is different for inhibited and uninhibited corrosive media. Its value is higher in the inhibited medium since the inhibitor decreases the rate of the corrosion process. Polarisation resistance can be estimated from slope analysis of linear polarization curves. Using $R_p$ values for inhibited and uninhibited media, percentage of corrosion inhibition efficiency can be calculated as,

$$\eta_{\mathrm{R_p}}\% = \frac{\mathrm{R'_p} - \mathrm{R_p}}{\mathrm{R'_p}} \mathrm{X100} \tag{33}$$

where $R'_p$ and $R_p$ are the polarization resistance values in the presence and absence of inhibitor, respectively.

***Electrochemical noise measurements***

Electrochemical noise (ECN) measurement is mainly used in corrosion inhibition analysis introduced by Iverson[36]. Electrochemical noise denotes current and potential fluctuations. This modern technique is widely accepted in corrosion inhibition analysis because a corroding metal at open circuit potential ($E_{OCP}$) can create random electrochemical noises since fluctuations are steady-state at the metal-solution interface. So, ECN measurements help to determine metal corrosion at $E_{OCP}$ without any external potential. Random current and potential noise signals derived from corrosion processes can be applied to investigate the corrosion rate. Fig. 1.11a shows the current noise vs time plot. Corrosion mechanism can be evaluated using the pitting index value. Fig. 1.11b shows the pitting index curve. ECN signals can measure either separately or simultaneously. In separate measurements, either potential or current noise is analyzed at a particular time, whereas, in simultaneous measurement, both noise signals are analyzed at the same time. Potential noise can be interpreted from the potential between a working electrode and a zero-noise reference electrode or two similarly working electrodes, whereas current noise can be analyzed from the current between a working electrode and a counter electrode or between two similarly working electrodes in separate measurement. Simultaneous measurement is more advantageous since it employs a three-electrode assembly. Current noise is analyzed between a working electrode and a counter electrode, and potential noise is analyzed between a working electrode and a reference electrode.

There are two methods for ascertaining ECN data. 1) Frequency domain analysis, 2) Time-domain statistical method

### ❖ ***Frequency domain analysis***

Sum of various sinusoidal signals of relative phase, periodicity and amplitude give the waveform of any complexity. That is the fundamental concept of frequency domain analysis. An illustration of a time depending process is referred to as a spectrum in frequency domain analysis. An important parameter derived from this analysis is the power spectral density (PSD)[37]. Fig. 1.11c shows the PSD plot. It plots the logarithm of spectral power of potential or current Vs logarithm of the frequency. PSD doesn't affect time and signal statistics. Greater amplitude of potential and current noise increased the localized corrosion of metal.

### ❖ ***Time-domain statistical methods***

ECN data can be rendered as a spectrum in terms of frequency through auto-correlation of the time-domain data[38]. This can be made possible by two mathematical approaches 1) Fast Fourier transform (FFT) and 2) Maximum entropy method (MEM).

#### *Fast Fourier transform*

Fast Fourier transform (FFT) method works based on previously existing algorithms. Complex Fourier series can be analyzed using this faster machine calculation method. FFT method adopts discrete Fourier transform properties. FFT analysis is associated with two main problems as leakage and aliasing[39]. Leakage is due to the periodicity of finite time records in Fourier transform outputs. Too slow sampling rate causes aliasing.

#### *Maximum entropy method*

Even though Fourier transform is a prominent method among all spectral analysis methods, it is proper for only long record lengths. If the record length is small, then the spectral resolution is weak. In such situations, resolution can be intensified by applying the maximum entropy method proposed by Burg[40]. In this method, the auto-correlation function gets extrapolated, and the entropy of the probability density function gets maximized. Thus, MEM is a data-dependent and nonlinear method widely operating in science and technology.

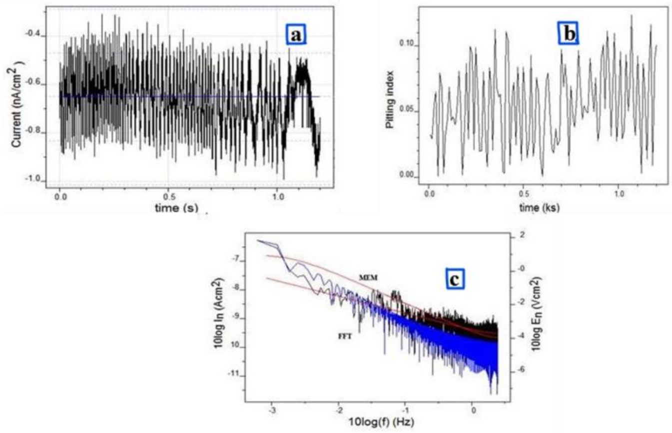


Fig. 1.11: a) Current noise vs time plot b) Pitting index curve c) PSD plot

## *Adsorption isotherms*

Adsorption is the primary phenomenon observed in the inhibition action of inhibitors. Interaction between inhibitor molecules and the metal surface can be explained by adsorption isotherms perfectly[41]. Organic inhibitors affect anodic and/or cathodic corrosion processes after removing water molecules from the metal surface. Displacement of the water molecules and attachment of inhibitor molecules on the metal surface are determined by disturbing cathodic or anodic reactions or both. This can be achieved by developing a diffusion barrier or hindering reaction sites[42, 43, 44]. Different types of adsorption isotherms can demonstrate the properties of inhibitor molecules adsorbed on the metal surface, such as chemical composition, temperature and interfacial electrochemical potential between metal and solution[45].

### ❖ *Langmuir adsorption isotherm*

Langmuir adsorption isotherm can be given by,

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{34}$$

where $\theta$ is the extent of occupancy of adsorbed sites, C signifies the concentration, and $K_{ads}$ implies the adsorption equilibrium constant.

This model explains the extent of occupancy of adsorbed sites by adsorbed molecules for a certain temperature and pressure of adsorbate[46]. According to Langmuir adsorption isotherm, there are many similar adsorption sites and little chance for lateral interaction.

- ***Freundlich adsorption isotherm***

It is commonly used in the determination of multisite adsorption for rough surfaces. The equation can represent it,

$$\theta = K_{ads} C \tag{35}$$

It is more suitable for rough surfaces than Langmuir adsorption isotherm[47].

- ***Temkin adsorption isotherm***

This model considers indirect adsorbate-adsorbate interactions on adsorption isotherms. It can be expressed as,

$$e^{f\theta} = K_{ads} C \tag{36}$$

where f denotes the molecular interaction constant.

- ***Frumkin adsorption isotherm***

This model supposes the multilayer adsorption of inhibitor molecules where there is an adsorbate-adsorbent interaction. It can be indicated as,

$$\frac{\theta}{1-\theta} \exp(f\theta) = K_{ads} C \tag{37}$$

*El-Awady adsorption isotherm*

This model can be explained by the equation,

$$\log \frac{\theta}{1-\theta} = \log K + y \log C \tag{38}$$

where $K_{ads} = K^{1/y}$ , (39)

y denotes the number of active sites. If 1/y<1, then it is multilayer adsorption, whereas if 1/y>1, then it is coverage of adsorbed molecules in more than one active site.

❖ ***Florry-huggin isotherm***

Florry-huggin isotherm is given by the following equation,

$$\log\frac{\theta}{C} = \log K_{ads} + \chi\log(1-\theta) \quad (40)$$

where $\chi$ is the polymer-solvent interaction parameter.

***Temperature studies***

Stability of the protective film of an inhibitor by adsorption on the metal surface can be described by performing temperature studies at elevated temperatures[48]. Various corrosion thermodynamic parameters such as entropy of corrosion ($\Delta S^*$), enthalpy of corrosion ($\Delta H^*$), activation energy for decay (with the electrical charge on the metal surface) and Arrhenius parameter (A) can be investigated by applying Arrhenius equation. Rate of corrosion and activation energy for corrosion is related in Arrhenius equation as,

$$K = A\exp\left(\frac{-E_a}{RT}\right) \quad (41)$$

where K represents the rate of corrosion, A is the pre-exponential factor known as Arrhenius parameter, $E_a$ denotes the activation energy for corrosion, R is gas constant, and T is the temperature. When we plot a graph between log K and 1000/T, we get a straight line with a slope $\frac{-E_a}{2.303R}$ and intercept of log A.

Transition state theory helps to obtain $\Delta S^*$ and $\Delta H^*$ values[49], which is given by the following equations,

$$K = \left(\frac{RT}{Nh}\right)\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(\frac{-\Delta H^*}{RT}\right) \quad (42)$$

where N denotes Avagadro number and h gives Planck’s constant.

This equation can be rearranged into logarithmic form as,

$$\log\frac{K}{T} = \log\frac{R}{Nh} + \frac{\Delta S^*}{2.303R} - \frac{\Delta H^*}{2.303RT} \qquad (43)$$

When we plot a graph between log K/T and 1/T, we get a straight line with a slope $\frac{-\Delta H^*}{2.303R}$ and intercept of $\log\frac{R}{Nh} + \frac{\Delta S^*}{2.303R}$ . From the slope and intercept, we can estimate the enthalpy and entropy of corrosion.

If the rate of corrosion increases as temperature increases, it may conclude that the nature of adsorption by the inhibitor is just physical adsorption. Stability of the adsorbed layer degrades at elevated temperatures. Or it can be said that the rate of desorption increases at elevated temperatures. If the adsorbed layer doesn't affect at higher temperatures, it may be chemisorption. When the activation energy of corrosion increases with inhibitor concentration, it can be said that the energy barrier for corrosion grows as possible[50]. It also emphasizes the existence of a complex compound formed by the interaction between the inhibitor and metal. Positive value of enthalpy of corrosion describes the endothermic character of the metal corrosion process. Negative values of the entropy of activation for corrosion mention a decrease in randomness for the activated complex, compared to the reactants that lead to a high corrosion rate. If the disorderliness of the activated complex increases with inhibitor concentration and $\Delta S^*$ becomes positive values, it causes the prevention of metal corrosion at high rates.

### ***Scanning electron microscopy (SEM)***

Scanning electron microscopy (SEM) is a non-destructive method to examine the surfaces and cross-sections with a resolution at micron and nanometer levels. It is practical to gather facts about surface properties like crystalline nature, chemical composition, electrical behaviour, etc. When a high energy electron beam passes through a sample surface, emerging particles like electrons, X-rays and photons, etc., provide the surface's character. That is the basis of SEM.

SEM is supposed to be a valuable tool for corrosion inhibition studies. SEM image of a metal surface can distinguish between the surface morphology of corroded and non-corroded metals evidently. The mechanism of corrosion inhibition can prove by recording SEM images of metals exposed in the aggressive medium in the presence and absence of inhibitors because inhibitors may form a protective film on the metal surface[51].

### *Atomic force microscopy (AFM)*

AFM is a well-known technique in which the surface topography of a sample can be explored at the microstructure level. So, it is widely employed in corrosion inhibition studies to establish barrier film formation on the metal surface.

AFM measures the force between a sharp probe and a sample surface at a minimum distance by touching the AFM tip on the surface and gives a 3D image of the surface on a nanoscale. The significant interactions between AFM tip and sample surface are van der Waals interactions[52]. Contact mode, tapping mode and non-contact mode are three imaging modes in AFM. Depending on the surface characteristics such as hardness, stickiness etc., the operating mode can be selected. Surface roughness parameters such as average roughness ($R_a$), root mean square roughness ($R_q$), and maximum peak-to-peak height ($R_{pp}$), which specify the topography of surfaces, are available from the AFM technique. Surface roughness parameters for the inhibited metal differ from the bare metal and the metal exposed in the aggressive medium. This reinforces the adsorption of inhibitor molecules on the metal surface in the corrosion reaction.

### *Quantum mechanical calculations*

Quantum mechanical calculations can achieve interactions of compounds at the molecular level. It can simply investigate chemical problems on a computer because quantum mechanical calculations provide information about molecular geometry such as bond lengths, angles, dihedrals, molecular energies, transition states, and chemical reactivity. Attainment of these problems is through the selection of different methods of computational chemistry. There are five broad classes of computational chemistry methods.

- Molecular mechanics (MM): It is a ball and spring model. Here ball indicates atoms, and spring represents the bond between them. So, a molecule can be considered as a collection of balls connected by springs. We can compute the energy of a given molecule by providing the normal spring lengths and the angles between them and stretching and bending energy. We can also obtain the geometry of a molecule with the least energy, i.e. geometry optimization.
- Molecular dynamics calculations: It is based on the laws of molecular motion. For example, it can predict the movement of an enzyme because it changes shape with respect to the binding substrate. Similarly, the activity of a swarm of water molecules around a solute molecule can be estimated.
- Ab initio calculations: Ab initio is a Latin word that means "from first principles". It is mainly focused on the Schrodinger equation. The energy of a molecule and wave function can be provided from this method by solving the Schrodinger equation for a molecule. The wave function for a molecule gives information about the electron distribution. We can ascertain the polar behaviour and which parts of it are probably affected by nucleophiles or electrophiles.
- Semi-empirical (SE) calculations: It also depends on the Schrodinger equation. However, SE calculations can’t employ in the analysis of highly complicated integrals. Instead, this method benefits from a kind of library of integrals assembled by obtaining the most suitable experimental values for calculated

terms like geometry or energy. It is called "semi-empirical" because it is comprised of theory and experiment.

- ➢ Density functional calculations: Density functional theory (DFT) calculations depend on the Schrodinger equation, same as ab initio and SE calculations. But, it estimates electron distribution as a function of electron density directly without using wave function. That is the significant difference in DFT calculations from the other two.

Molecular structure of the inhibitor has a vital role in the determination of corrosion inhibition potency. Corrosion inhibition potency of organic inhibitors has been effectively correlated to molecular orbital (MO) energy levels by employing quantum mechanical calculations[53,54,55]. DFT calculations have been contributed to the calculation of parameters such as energies of HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), dipole moment (μ) etc., with sufficient accuracy. Mechanism of corrosion resistance can be demonstrated concerning HOMO-LUMO interaction between filled orbitals of inhibitor molecules and vacant orbitals of metal. Lower change in energy value ($\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$) is the benchmark for strong adsorption of inhibitor molecules on the metal surface. Ionization energy, electron affinity, chemical potential, electronegativity, hardness, and the number of transferred electrons are the typically obtained parameters using DFT.

- Ionization energy (I): Negative of the energy value of HOMO gives ionization energy. $\mathrm{I} = -\mathrm{E}_{\mathrm{HOMO}}$ (44)
- Electron affinity (A): Negative of the energy value of LUMO gives electron affinity. $\mathrm{A} = -\mathrm{E}_{\mathrm{LUMO}}$ (45)
- Electronegativity (χ): It can be obtained in terms of orbital energies as,

$$\chi = -\frac{(\mathrm{E}_{\mathrm{HOMO}} + \mathrm{E}_{\mathrm{LUMO}})}{2} \tag{46}$$

- Chemical potential (μ): It may express as the negative of the electronegativity. If the species is more electronegative, then energy drop is more, i.e. chemical potential decreases. So,

  $$\mu = -\chi \tag{47}$$

- Hardness ($\eta$): It measures the reduction in electronegativity when a minute electronic charge is added to it. If the value of the hardness of an inhibitor is smaller, then its inhibition efficiency is high.

  $$\eta = \frac{1}{2}(E_{LUMO} - E_{HOMO}) \tag{48}$$

- Number of transferred electrons (ΔN): The number of transferred electrons from the inhibitor molecule to the metal atoms can be calculated as[56],

  $$\Delta N = \frac{(\chi_{metal} - \chi_{inhibitor})}{2(\eta_{metal} + \eta_{inhibitor})} \tag{49}$$

### Natural organic inhibitors as a tool for metal corrosion inhibition

Plants are made up of phytochemicals. They are producing a large number of chemical constituents at a time. So, it is monotonous to isolate and separate the phytochemicals present in it. However, this difficulty can be overcome using advanced and sophisticated instrumental techniques like HPLC, GCMS etc.

Primary and secondary metabolites are major chemical compounds present in plants. Proteins, nucleic acids, lipids and carbohydrates belong to primary metabolites. Terpenoids, alkaloids and phenolics are the major secondary metabolites that are biosynthesized from primary metabolites. Secondary metabolites have broad applications in human lives, which can act as drugs, stimulants, functional foods, flavours, fragrances, natural insecticides and herbicides[57].

Terpenoids possess pharmacological characteristics like antibacterial, antiviral, anti-inflammatory, anticancer, anti-diabetic, etc. Alkaloids are the first isolated organic compounds from plants, known to be either medicinally beneficial or toxic. Flavonoids are polyphenols mainly found in the plant kingdom with bright and striking colours. Anthocyanins, flavones, flavonols and their derivatives like isoflavonoids, neoflavonoids belong to the flavonoids family. They are important for human health, such as antioxidant, antibacterial, antiviral etc. They also have wide applications in the food industry.

In recent years, green chemistry has been gaining traction in the research world, owing to a demand for chemical technologies and commercial products that are less toxic and generate less waste. One of the promising domains for applying green chemistry principles is the protection of metals from corrosion. Most industries work in an acidic environment, which causes metal corrosion, leading to metal loss. The best and favourable method to reduce metal degradation is the usage of corrosion inhibitors. Organic compounds with heteroatoms like N, O, S etc., in a conjugated system, have been commonly used as inhibitors and can interact with metal either by chemisorption or physisorption. The adsorptive layer formed on the metal surface protects from the acidic solution and thereby minimizing corrosion. Due to eco-friendliness, low cost, readily available and renewable sources of material, natural products like plant extracts can be used as green corrosion inhibitors. Several plant-based extracts successfully inhibited the corrosion of metals in corrosive environments. These are listed in Table 1.1 and structures of active constituents listed in Table 1.1 are given in Fig. 1.12 and Fig. 1.13.

K. K. Anupama et al. have been studied the effect of corrosion behaviour of methanolic extracts of leaves of *Ruta graveolens* (RGE) in 1 M HCl for mild steel using gravimetric and electrochemical techniques in 2016[48]. RGE exhibited 98% inhibition efficiency at 4 v/v% from EIS studies. Theoretical calculations were also proved with experimental results. Rutin is the active component present in RGE that supported the adsorption mechanism of the extract on the mild steel surface.

Table 1.1: List of natural organic inhibitors with their active constituents, material/medium used and inhibition efficiency (IE%)

| Inhibitors | Active constituents | Material/medium | IE% |
|---|---|---|---|
| *Ruta graveolens* | 1) Rutin | Mild steel/1 M HCl | 98.00 |
| *Tinospora cordifolia* | 2) Borapetoside F | Low-carbon steel/ 0.5 M $H_2SO_4$ | 87.18 |
| *Terminalia chebula* | 3a) Gallic acid<br>3b) Methyl gallate | Low-carbon steel/ 0.5 M $H_2SO_4$ | 94.07 |
| *Ficus religiosa* | 4a) Myricetin<br>4b) Serotonin<br>4c) Campesterol | Mild steel/ 0.5 M $H_2SO_4$ | 92.26 |
| *Asparagus racemosus* | 5) Sarsasapogenin | Mild steel/0.5 M $H_2SO_4$ | 93.25 |
| *Achyranthes aspera* | 6) Oleanolic acid | Mild steel/0.5 M $H_2SO_4$ | 90.79 |
| Aloe vera | 7a) Anthraquinone<br>7b) p-Coumaric acid<br>7c) Calleic acid<br>7d) Ferulic acid | Mild steel/0.5 M $H_2SO_4$<br>Stainless Steel/0.5 M $H_2SO_4$ | 88.90<br>99.10 |
| *Cinnamomum verum* | 8) Eugenol | Mild steel/1 M HCl<br>Mild steel/0.5 M $H_2SO_4$ | 99.00<br>96.55 |
| *Chlorophytum borivlianum* | 9) Saponins | Mild steel/1 M HCl<br>Mild steel/ 0.5 M $H_2SO_4$ | 90.00<br>83.00 |
| *Punica grantum* | 10a) Pelargonidin<br>10b) Pelletierine<br>10c) Gallic acid<br>10d) Ellargic acid | Mild steel/1 M HCl<br>Mild steel/0.5 M $H_2SO_4$ | 80.60<br>91.00 |
| *Allium sativum* | 11) Allicin | Mild steel/well water | 90.00 |
| *Geissospermum laeve* | 12) Geissospermine | C38 steel/1 M HCl | 92.00 |
| Lemongrass extract | 13a) Neral<br>13b) Geranial<br>13c) β- myrcene<br>13d) Nerol | Carbon steel/produced oilfield water | 58.19 |
| *Strychnos nuxvomica*, *Piper longum* and *Mucuna pruriens* | 14a) Brucine<br>14b) Piperine<br>14c) L-DOPA | Copper/3 M $HNO_3$ | 91.60<br>80.00<br>71.60 |
| olive leaves | 15a) Hydroxylyrosol<br>15b) Oleuropein | Carbon steel/2 M HCl | 93.00 |
| Rice hulls | 16) β-Sitosterol | Mild steel/1 M $H_2SO_4$ | 95.00 |
| *Saraca ashoka* | 17) Epicatechin | Mild steel/0.5 M $H_2SO_4$ | 95.48 |
| *Musa paradisica* | 18) Gallocatechin | Mild steel/1 M HCl | 89.00 |
| Fennel essential oil | 19a) Limonene<br>19b) β-Pinene | Carbon steel/1 M HCl | 77.00 |
| Cinnamon essential oil | 20a) E-Cinnamaldehyde<br>20b) δ – Cadinene<br>20c) β- Cubebene | Copper/0.5 M $H_2SO_4$ | 87.24 |

In 2020, Akhil Saxena and coworkers investigated that ethanol extracts of fruits of *Tinospora cordifolia* showed 87.18% effectiveness at 500 mg/L inhibitor concentration using potentiodynamic polarization studies[58]. Weight loss, EIS studies, SEM and AFM analyses were also supported for their corrosion effectiveness. Borapetoside F is the chief component that leads to adsorption on the metal surface following the Langmuir adsorption isotherm. In 2019, inhibiting power of ethanol extracts of seeds of *Terminalia chebula* has been studied by Akhil Saxena et al. using electrochemical and surface morphological studies[59]. It exhibited 94.07% inhibition potency at 500 mg/L inhibitor concentration in 0.5 M $H_2SO_4$ for low-carbon steel from potentiodynamic polarization studies. DFT calculations based on the active constituents, gallic acid and methyl gallate, were observed with experimental results.

In 2018, Rajesh Haldhar and coworkers reported that ethanol extracts of the fruits of *Ficus religiosa* showed an extreme inhibition efficiency of 92.26% at 500 mg/L in 0.5 M $H_2SO_4$ for mild steel using electrochemical and gravimetric estimations[60]. The major components present in the extract are myricetin, serotonin, and campesterol, which cause adsorption film on the metal surface, thereby decreasing the corrosion rate. Akhil Saxena et al. suggested that ethanol extract of fruits of *Achyranthes aspera* exhibited 90.79% protecting power at 500 mg/L in 0.5 M $H_2SO_4$ for mild steel using potentiodynamic polarization studies in 2018[61]. They investigated that the adsorption behaviour of oleanolic acid, an active component present in the extract, cause a decrease in corrosion rate. Inhibition effect of colourless liquid extract from aloe vera in 0.5 M $H_2SO_4$ for mild steel and stainless steel was reported by A. A. Ayoola et al. in 2020[62]. It revealed that aloe vera extract showed a maximum protection capacity of 88.9% for mild steel and 99.1% for stainless steel at 10 v/v%. In 2018, K. K. Anupama et al. reported that ethanol extract of leaves of *Cinnamomum verum* exhibited a maximum inhibition power of

99.73% in 1 M HCl and 96.55% in 0.5 M $H_2SO_4$ using potentiodynamic polarization studies[63].

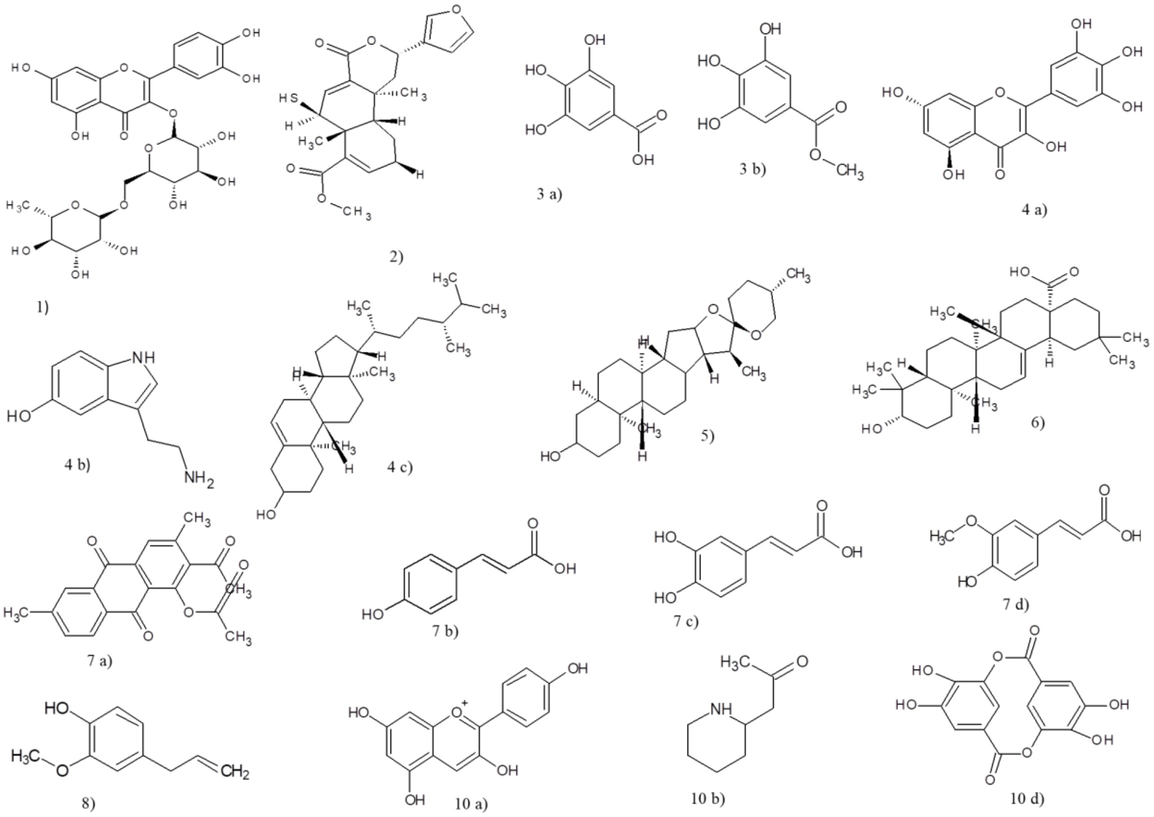


Fig. 1.12: Structures of active constituents of natural organic corrosion inhibitors (1-10)

In 2013, Gopalji et al. suggested that aqueous extracts of roots of *Chlorophytum borivlianum* showed an extreme inhibition effect of 90% and 83% in 1 M HCl and 0.5 M $H_2SO_4$ respectively in weight loss measurements[64]. In 2012, Maduabuchi A. Chidiebere et al. showed that ethanol extract of seeds of *Punica grantum* exhibited a maximum inhibition potency of 80.6% and 91% in 1 M HCl and 0.5 M $H_2SO_4$, respectively, using EIS studies[65]. In 2018, N. Karthiga and coworkers reported that aqueous extract of garlic exhibited 90% inhibition efficiency in well water for mild steel in weight loss measurements[66]. Inhibition ability of alkaloid extract of *Geissospermum laeve* in 1 M HCl with 100 mg/L for C38 steel was investigated by M. Faustin et al. in 2014[67]. It exhibited 92% inhibition power from weight loss measurements. In 2017, M. A. Deyab et al. suggested that water extract of lemongrass showed 58.19% protection power with

400 ppm concentration in produced oilfield water for carbon steel from weight loss measurements[68]. It was also supported by EIS studies, potentiodynamic studies and quantum chemical calculations. Savita and coworkers discovered that *Strychnos nuxvomica, Piper longum and Mucuna pruriens* seed extracts could act as a green inhibitor in 3 M $HNO_3$ for copper with the maximum corrosion resistance 91.60%, 80% and 71.6% respectively at 0.2 g/L from weight loss measurements in 2016[69].

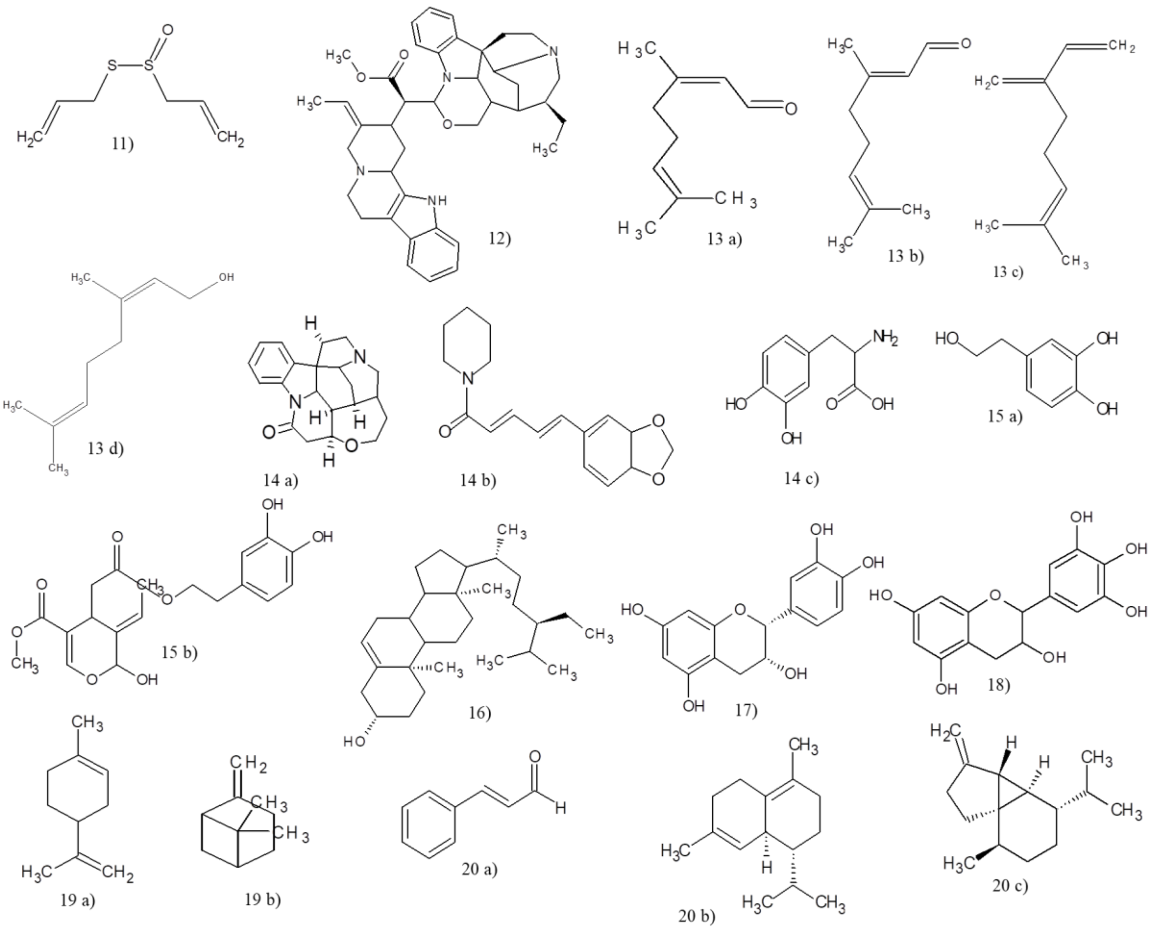


Fig. 1.13: Structures of active constituents of natural organic corrosion inhibitors (11-20)

A.Y. El-Etre has been conducted polarization techniques to evaluate the inhibiting capacity of aqueous extract of olive leaves. It exhibited an extreme corrosion inhibition efficacy of 93% in 2 M HCl for mild steel with 900 ppm inhibitor concentration in 2007[70]. In 2017, Mayakrishnan Prabakaran et al. reported that β-Sitosterol isolated from rice hulls revealed an extreme inhibition capacity of 95% in 1 M

$H_2SO_4$ for mild steel with 500 ppm inhibitor concentration from weight loss measurements[71]. In 2018, Akhil saxena and coworkers reported that ethanol extract of seeds of *Saraka ashoka* showed the best inhibition power of 95.48% at 100 mg/L inhibitor concentration in 0.5 M $H_2SO_4$ for mild steel from polarization measurements[72]. Gopal Ji et al. suggested that raw banana peel extract is a good green corrosion inhibitor with 89% protecting power in 1 M HCl for mild steel at 300 mg/L inhibitor concentration from EIS studies in 2014[73].

Performance of fennel essential oil as a corrosion inhibitor in 1 M HCl for carbon steel with 77% corrosion resistance power at 3 mL/L was studied by N. Lahhit et al. in 2011 using polarization studies[74]. In 2017, K. Dahmani et al. reported that cinnamon essential oil has 87.24% corrosion inhibition potency in 0.5 M $H_2SO_4$ for copper at 150 ppm inhibitor concentration from EIS calculations[75].

### Synthetic organic inhibitors as a tool for metal corrosion inhibition

Acid cleaning, oil and gas industries tremendously utilize synthetic organic inhibitors for inhibiting corrosion of metals, especially for iron and its alloys, like mild steel and carbon steel. This metal passivation is mainly through the phenomenon of adsorption. Adsorption film formed by organic inhibitors is more uniform and covered than those created by inorganic inhibitors. So, inorganic inhibitors cause localized corrosion on the metal surface. The most commonly observed organic inhibitors are heterocyclic compounds that possess heteroatoms such as sulfur, phosphorus, nitrogen and oxygen. The lone pair of electrons present in these heteroatoms involve in the adsorption mechanism. Table 1.2 shows some of the synthetic organic inhibitors used for metal corrosion, and Fig. 1.14 exhibits the structures of these synthetic organic inhibitors.

Table 1.2: List of synthetic organic corrosion inhibitors

| Authors | Synthetic organic inhibitor |
|---|---|
| A.M. Fekry et al. | 1a) 4-(4-methoxyphenyl)-6-(yridine-3-yl)-1H-pyrazolo[3,4-b]42yridine-3-amine<br>1b) 4-phenyl-6-(42yridine-3-yl)-1H-pyrazolo [3,4- b]42yridine-3-amine<br>1c) 6-(42yridine-3-yl)-4-(thiophen-2-yl)-1H-pyrazolo[3,4-b]42yridine-3-amine<br>1d) 4-(furan-2-yl)-6-(42yridine-3-yl)-1H-pyrazolo[3,4-b]42yridine-3-amine |
| Sutter et al. | 2a) Benzotriazole<br>2b) Mercaptobenzimidazole<br>2c) Mercaptobenzoxazole<br>2d) Mercaptobenzothiazole |
| Gurmeet Singh et al. | 3) 4,6-dihydroxypyrimidine |
| Ezhilarasi et al. | 4) 1-acetyl-4,5-dihydro-5-phenyl-3-(thiophen- 2yl) pyrazole |
| Dr. Mushtaq J. Meften | 5) 6,12,14-trithia-1,4,8,10-tetraaza-tricyclo [9.4.0.03,9] pentadeca-3(9),10-dien-2-one |
| A. S. Fouda et al. | 6a) 2-styrylbenzo[d] oxazole<br>6b) 4-(€-2-(benzo[d] oxazol-2-yl)vinyl)-N,N-dimethyl benzenamine<br>6c) 4-(€-2-(benzo[d]thiazol-2-yl)vinyl)-N,N-dimethyl benzenamine |
| J. Aljourani et al. | 7a) Benzimidazole<br>7b) 2-methylbenzimidazole<br>7c) 2-mercaptobenzimidazole |

A. M. Fekry et al. have been investigated the inhibiting capacity of some newly synthesized aromatic heterocyclic inhibitors for mild steel in 1 M $H_2SO_4$ using hydrogen evolution reaction and electrochemical techniques[76]. Sutter and coworkers have been studied the effect of four different aromatic heterocyclic inhibitors for copper corrosion, and they are characterized through their $C^{13}$ and $H^1$ NMR spectroscopy methods[77]. Applicability of dihydroxypyrimidine as a corrosion inhibitor for mild steel in 1 N phosphoric acid has been recorded by Gurmeet Singh and coworkers[78]. They observed the adsorption behaviour of inhibitors at different temperatures using electrochemical studies. All the inhibitors mentioned above are aromatic amine derivatives that develop an adsorption film on the metal surface by coordinating their non-bonding and $\pi$-electrons with vacant d-orbital of the metal surface.

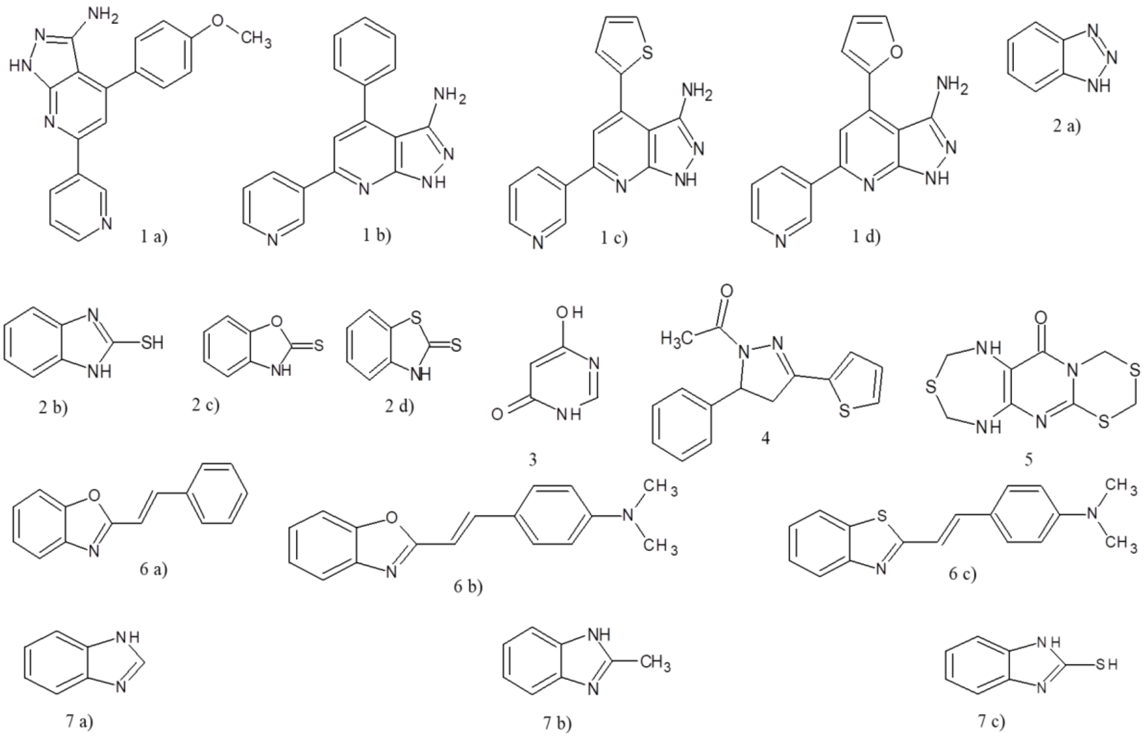


Fig. 1.14: Structures of synthetic organic corrosion inhibitors

Ezhilarasi et al. reported the effect of corrosion inhibition properties of a pyrazole based ionic liquid in 1 M HCl and 1 M $H_2SO_4$ on mild steel using weight loss and electrochemical techniques[79]. The structure of the inhibitor was characterized by FTIR, $^1$H NMR and $^{13}$C NMR. Dr Mushtaq J. Meften synthesized a new heterocyclic compound and characterized it by liquid chromatography, LC-MS, $^1$H NMR and $^{13}$C NMR[80]. He verified the applicability of the synthesized inhibitor as an anti-corrosive agent in 15% HCl on C38 carbon steel using the gravimetric method, gasometrical method, EIS, and X-ray diffraction (XRD) spectroscopy. Corrosion inhibition efficiency of three heterocyclic compounds for carbon steel in 1 M HCl has been analyzed by A.S. Fouda et al. using various physicochemical and electrochemical techniques[81]. J. Aljourani and coworkers have been studied the inhibition efficacy of some benzimidazole derivatives on carbon steel in 1 N HCl and 1 N $H_2SO_4$ using adsorption and electrochemical studies[82]. They also verified the synergistic effect of halide ions on inhibition efficiency when it adds with inhibitors.

**Schiff bases as a tool for metal corrosion inhibition**

Schiff bases accounted for their high inhibition efficiency among various synthetic organic inhibitors due to their electronic and structural properties. They can coordinate with the metal surface through $\pi$-electrons from double bonds and lone pairs of electrons from nitrogen. Many researchers reported that different types of Schiff base compounds could apply in corrosion inhibition processes. Table 1.3 shows some of the Schiff bases used as inhibitors for metal corrosion in acidic media and Fig. 1.15 exhibits and their structures.

Shaju K. S et al. have been investigated the effect of corrosion resistance offered by a polynuclear Schiff base compound in 0.5 M $H_2SO_4$ on mild steel employing weight loss measurements, EIS and potentiodynamic polarization studies[83]. They also pointed out that the efficiency was enhanced by adding potassium iodide with inhibitor, and adsorption studies proved it. Nimmy Kuriakose and coworkers have been studied the corrosion inhibition behaviour of a Schiff base derived from the condensation reaction between thiophene-2-carbaldehyde and tryptophan in 1 M HCl for mild steel corrosion using gravimetric and electrochemical methods[84]. Synthesis of some novel Schiff base compounds and anti-corrosive behaviour of those inhibitors in 1 M HCl on mild steel has been conducted experimentally and theoretically by Hany M. Abd El-Lateef et al.[85]

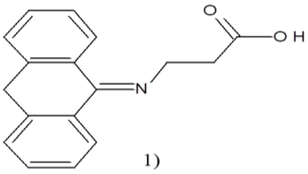
Aby Paul and coworkers discovered that a Schiff base derived from 3-Formylindole and 4-aminobenzoic acid has potential for corrosion inhibition in 1 M HCl on mild steel and copper by employing weight loss measurements, EIS and potentiodynamic polarization studies[86]. Adsorption mechanism of the synthesised inhibitor was proved by calculating thermodynamic parameters.

Table 1.3: List of Schiff base corrosion inhibitors

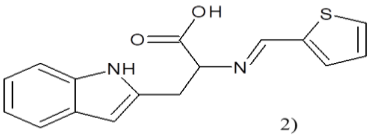
| Authors | Schiff base |
|---|---|
| Shaju K. S et al. | 1) Anthracene-9(10H)-one-3-aminopropanoic acid |
| Nimmy Kuriakose et al. | 2) Thiophene-2-carbaldehyde tryptophan |
| Hany M.Abd El-Lateef et al. | 3a) Sodium 3-[{[1-carboxy-3-(methylthio)propyl] imino}methyl]-4-hydroxybenzenesulfonate<br>3b) Sodium 3-{[(1-carboxy-2-phenylethyl) imino]methyl}-4-hydroxybenzenesulfonate |
| Aby Paul et al. | 4) 3-formylindole-4-aminobenzoic acid |
| Yue Meng et al. | 5a) 3-pyridine carboxaldehyde-4-phenyl thiosemicarbazide<br>5b) 4-pyridine carboxaldehyde-4-phenyl thiosemicarbazide |
| Parul Doharea et al. | 6a) $N^2$,$N^6$-bis(4-ethylbenzylidene)pyridine-2,6-diamine<br>6b) $N^2$,$N^6$-dibenzylidenepyridine-2,6-diamine<br>6c) $N^2$,$N^6$-bis(4-nitrobenzylidene)pyridine-2,6-diamin |
| Sam John et al. | 7a) Anisoin-N(4)-methyl(phenyl)thiosemicarbazone<br>7b) Furoin-N(4)-methyl(phenyl)thiosemicarbazone |
| A. Yurt et al. | 8a) 2-((1E)-2-aza-2-pyrimidine-2-ylvinyl) thiophene<br>8b) 2-((1Z)-1-aza-2-(2-pyridyl)vinyl) pyrimidine<br>8c) 2-((1E)-2-aza-2-(1,3-thiazol-2-yl)vinyl) thiophene<br>8d) 2-((1Z)-1-aza-2-(2-thienyl)vinyl) benzothiazole |
| M. G. Hosseini et al. | 9a) N,N-ethylen-bis(salicylidenimine)<br>9b) N,N-isopropylien-bis(salicylidenimine)<br>9c) N-acetylacetone imine N-(2-hydroxybenzophenone imine)ortho-Phenylen |
| C. Sini Varghese et al. | 10a) 2-pyridine carbaldehyde oxime<br>10b) 3-pyridine carbaldehyde oxime |

Yue Meng et al. synthesized two novel pyridine Schiff base derivatives[87]. They accounted for the corrosion inhibition property of the synthesized compound in 1 M HCl on mild steel, including experimental and theoretical studies. SEM and X-ray photoelectron spectroscopy analyses were employed to justify the formation of adsorption film on the mild steel surface. Synthesis, characterization and corrosion inhibition studies of three pyridine-based Schiff bases in 1 M HCl for mild steel has been carried out by Parul Dohare et al., incorporating electrochemical and theoretical studies[88]. DFT calculations and Monte Carlo simulations were conducted to correlate metal-inhibitor interaction. Sam John and coworkers have been investigated the corrosion inhibition ability of two N(4)-substituted thiosemicarbazone compounds in 1 M HCl for mild steel using weight loss, electrochemical and surface morphological studies[89]. The mechanism of interaction between the inhibitor and mild steel was further justified by molecular dynamic simulations. Potentiodynamic polarization and ac impedance techniques have been conducted to evaluate the inhibition efficiency of some Schiff bases in 1 M HCl on carbon steel by A. Yurt et al.[90] Polarisation studies were revealed that examined Schiff bases could act as an anodic inhibitor.

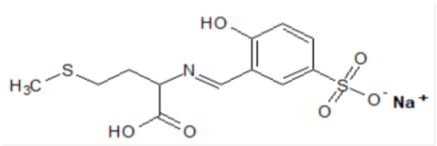
M. G. Hosseini et al. have been investigated the effect of protecting power of three new Schiff bases in 0.5 M $H_2SO_4$ for mild steel using EIS and Tafel polarization studies[91]. Thermodynamic calculations were proved that the nature of adsorption was physisorption. Electrochemical and gravimetric evaluations on anti-corrosive properties of pyridine-carbaldehyde derivatives in 1 M HCl on carbon steel were carried out by C. Sini Varghese et al[92]. Mechanism of adsorption was determined by calculating thermodynamic parameters.



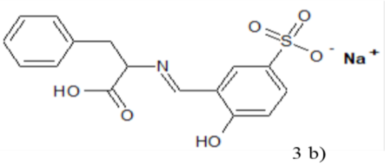
1)



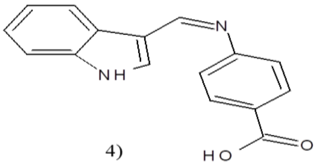
2)



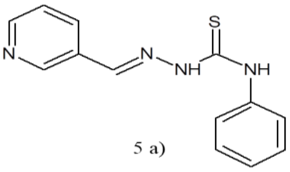
3 a)



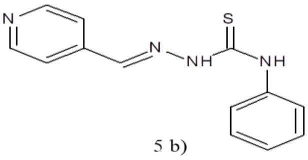
3 b)



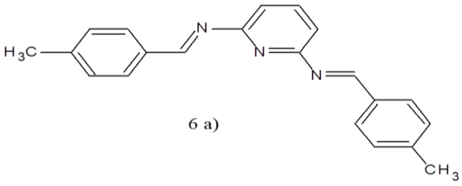
4)



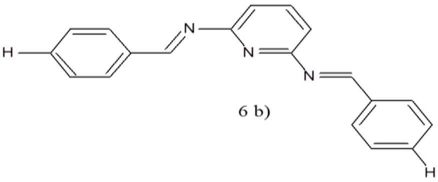
5 a)



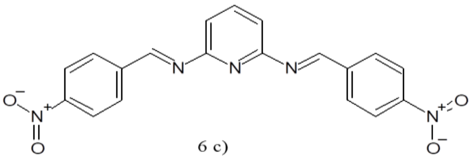
5 b)



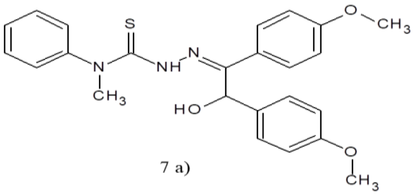
6 a)



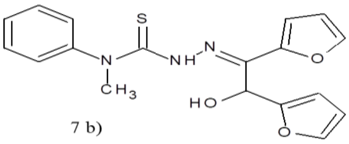
6 b)



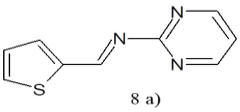
6 c)



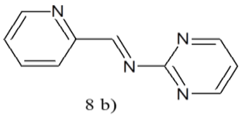
7 a)



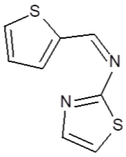
7 b)



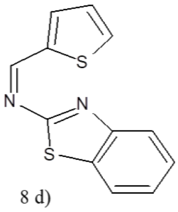
8 a)



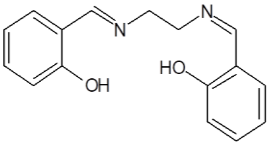
8 b)



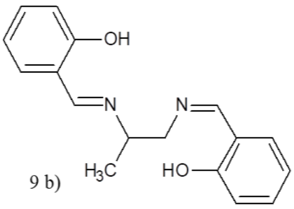
8 c)



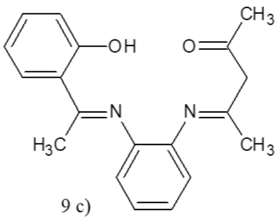
8 d)



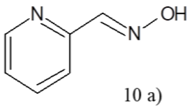
9 a)



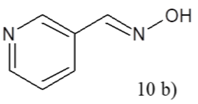
9 b)



9 c)



10 a)



10 b)

Fig. 1.15: Structures of Schiff base corrosion inhibitors

**Schiff bases as a tool for microbial induced corrosion inhibition**

Microbial induced corrosion (MIC) is the destruction of a metal by the activity of living organisms either directly by enhancing the electrochemical reactions or indirectly because of their metabolic products. Various environments such as soil, natural waters, seawater, natural petroleum products and oil emulsion cutting fluids encounter the difficulties of corrosion by such biological activity. It is surprisingly high in the contribution of microbial corrosion loss towards total corrosion loss. MIC is termed for corrosion by the occupancy and activities of microbes within biofilms at metal surfaces[93]. The term 'biofilm' was introduced in 1978[94]. By definition, it is a "matrix-enclosed bacterial populations" attached to one another or surfaces. Biofilms are a vital part of the destruction process in MIC. Biofilms are formed by creating extracellular polymeric substances (EPS) such as lipids, polysaccharides, nucleic acids, and proteins[95]. The proximity of biofilms to metal surfaces generates an electrochemical disturbance that allows electron transfer at the anode. Locales at which microbes set apart the metal is mentioned as an anode. The cathodic sites are places of oxygen availability at which corrosion could occur. So, it is difficult to deal with biofilm in mechanical systems.

MIC applies to metals and non-metallic surfaces such as concrete and causes drastic industry losses. MIC has attracted much research interest and attention from researchers and engineers in the last few years, especially with developing new and sophisticated surface morphological and electrochemical techniques that can determine the influence of microorganisms on electrochemical reactions and corrosion chemistry.

Most of the microorganisms causing microbial corrosion are chemotrophs that use chemicals as an energy source[96]. They are as follows:

- Sulphate reducing bacteria (SRB)
- Sulphur oxidizing bacteria (SOB)

- Iron oxidizing/depositing bacteria (IB)
- Manganese oxidizing/depositing bacteria (MnB)

Micro-organisms operate in different ways:

- By generating sludge and deposits which causes crevice corrosion;
- By developing corrosive environments through their metabolic products, or by demolishing corrosion inhibitors;
- By quickest interaction with the corrosion reactions.

Some of the aerobic bacteria like the sulphur oxidisers and the iron bacteria are capable of producing aggressive corrosion environments. For example, the sulphur oxidisers mainly observed in metalliferous mines, oil fields etc., can oxidise elemental sulphur or sulphur containing compounds to $H_2SO_4$[97]. They proliferate in acidic environments and can generate deposits of sulphuric acid concentrations up to 5 wt%. The sulphur-oxidising bacteria (SOB) cause a mass loss in metals, alloys and even in non-metals, even though the mechanism of corrosion is just acid attack. *Thiobacillus ferrooxidans* is SOB, can form sulfuric acid utilizing sulfur or sulphide.

Another class of aerobic bacteria is the iron bacteria which are mainly found in soil waters and supply waters oxidise ferrous iron to ferric hydroxide precipitates. They tend to develop tubercles on the steel surface of supply pipes. It may cause crevice corrosion in steel pipes. It also made a suitable habitat for the anaerobic bacteria. Iron bacteria can oxidize and/or deposit iron oxides extracellularly or intracellularly[98]. Iron bacteria derive energy from Fe(II) oxidation process with Fe(III). *Pseudomicrobium sp.* and *Gallionella sp*. are fundamental species that belong to iron-oxidizing bacteria. These species can oxidize $Mn^{2+}$ to $Mn^{3+}$ also. Iron reducing bacteria causes depolarization of mild steel surface by modifying the protective oxide film on it.

Another class of bacteria are acid-producing bacteria (APB) which creates the most harmful metabolites, i.e., acids. For example, acetic and butyric acids. APB can readily be confined under the biofilms and generate acids leads to under film corrosion[99]. One of the acetic acid-producing bacteria, *Acetobacter aceti,* facilitated the corrosion process by destroying a protective calcareous film formed due to cathodic polarization. Similarly, *Thiobacillus* can produce sulfuric acid that is hugely corrosive. There are three ways to enhance corrosion for the produced acids:

(1) Prone to more cathodic reactants.

(2) Coordination with metal ions.

(3) Eradicating the passive film and obstructing the passivation.

Sulphate-reducing bacteria (SRB) are a group of anaerobic bacteria that reduce dissolved sulphate to sulphide by ingesting hydrogen and bringing about corrosion to steel frameworks[100]. They can double the effect of metal corrosion. The corrosion rate is stimulated through the cathodic reaction of the corrosion couple, which is achieved via a better mechanism of elimination of hydrogen from the metal surface. Or the corrosion process can also be enhanced from the sulphide layers created from their metabolic products. SRB can be considered the predominant supporter of MIC due to their metabolic activity to provide $H_2S$. Mechanism of anaerobic bacterial corrosion is as follows:

Anodic reaction: $4\mathrm{Fe} \rightarrow 4\mathrm{Fe}^{2+} + 8\mathrm{e}^-$

Dissociation of water: $8\mathrm{H_2O} \rightarrow 8\mathrm{H}^+ + \mathrm{OH}^-$

Cathodic reaction: $8\mathrm{H}^+ + 8\mathrm{e}^- \rightarrow 8\mathrm{H}$

Cathodic depolarization: $\mathrm{SO_4^{2-}} + 8\mathrm{H} \rightarrow \mathrm{S}^{2-} + 4\mathrm{H_2O}$

$\mathrm{Fe}^{2+} + \mathrm{S}^{2-} \rightarrow \mathrm{FeS}$

Corrosion products: $3\mathrm{Fe}^{2+} + 6\mathrm{OH}^- \rightarrow 3\mathrm{Fe(OH)_2}$

Overall reaction: $4\mathrm{Fe} + \mathrm{SO_4^{2-}} + 4\mathrm{H_2O} \rightarrow 3\mathrm{Fe(OH)_2} + \mathrm{FeS} + 2\mathrm{OH^-}$

Based on the nature of the soil, sulphate-reducing and sulphur-oxidising bacteria can take effect periodically. Rainy season enhances the multiplication of sulphate-reducing bacteria where the soil is moistened and doesn't expose it to air circulation. In contrast, dry season prospers the growth of sulphur oxidisers by oxidising the sulphide compounds produced in metabolism to sulphuric acid. It leads to the immense destruction of buried metal structures.

Manganese oxidizing bacteria can catalyze Mn(II) oxidation to MnO. It resulted in the growth of visible and easily noticeable extracellular deposits of insoluble manganese oxides[101]. Various organisms tend to catalyse manganese oxidation, such as bacteria, fungi, algae and even eukaryotes. Two Mn(II) oxidation mechanisms by bacteria are 1) indirect and 2) direct. There are free radicals for hydrogen peroxide, superoxide, and OH radicals in the indirect method. In the direct method, Mn(II) oxidation is made possible by Mn-binding compounds like proteins, cell wall compounds and Mn oxidizing enzymes.

Slime-forming bacteria belong to either aerobic or anaerobic. They lead to creating differential aeration cells and capsules on the biofilm surface. The slime capsules can protect the biomass formed inner side from the application of antimicrobial compounds.

Microorganisms enhance metal corrosion by interfering at the interface between the metal and the electrolyte. They are exposed to the atmosphere by attaching themselves to metal surfaces, then colonizing, multiplying, and forming a biofilm. Biofilm contains metabolites of microbes and their extracellular polymeric substance (EPS). Biofilm formation leads to change in pH, dissolved oxygen, nutrient contents, temperature, and pressure, which cause the MIC of metals and alloys. 20%–25% of the overall financial loss of corrosion was due to MIC. MIC is fundamentally an electrochemical phenomenon, the same as other types of corrosion. All structural materials associated with the water and soil are possible to suffer from MIC. Among these factors, water is essential for the life of microorganisms, and hence, water is predominant to occur MIC. Mainly, it has been explained that microbes in any condition, such as temperature, salinity, nutrients, etc., cause localized corrosion.

***MIC inhibition strategies***

According to the types of apparatus and proper maintenance required, MIC mitigation has different strategies (Fig.1.16).

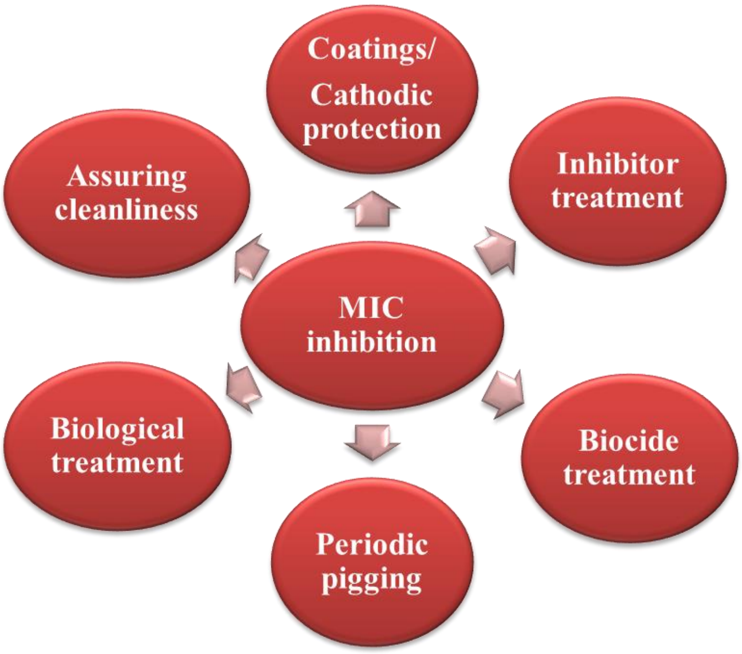


Fig. 1.16: Schematic representation of MIC inhibition strategies

❖ ***Periodic pigging***

It is a mechanical strategy used in oil and gas pipelines to mitigate MIC. Usually, in pipelines, a mechanical pig carrying compact plastic plates is applied to empty garbage from the inner parts of the pipe prior to injection of biocide. This mitigating strategy removes bits of biofilm and maintains solid particles, encouraging the immediate activity of biocides[102,103]. Pigging is a non-harmful method for the review and washing of pipelines. But, it is not an excellent strategy to inhibit MIC.

❖ ***Cleanliness***

An immaculate operational state that does not enter solids, oxygen, waste, polluted waters etc., Compatible throw out of solid waste, washing, and drying are various processes involved in this method. It is a simple technique to preclude or at least control internal pollution.

❖ ***Cathodic protection and coatings***

It is mainly the least laborious, economically sound, and most effective MIC inhibition method for vessels and tanks. In underground pipelines, removal of covering is the root cause of corrosion in this area. Polymeric compounds are the chief constituents of industrial coatings[104]. Polystyrene and epoxy resin are highly stable industrial coatings towards microbial attack. Coatings are able to defend aggressive synthetic compounds, which are produced by some acid-producing bacteria that may cause corrosion.

❖ ***Biological treatment***

It is the most advanced method for inhibiting MIC, i.e. applying particular bacteria to inhibit the growth of the bacteria which cause MIC. Nitrate reducing bacteria are used to fight against SRB, which creates corrosion.

❖ ***Biocides/Inhibitors***

Corrosion inhibitors are chemicals used to considerably decrease the overall corrosion rate by affecting anodic, cathodic, or both types of reactions. In terms of MIC, these chemicals are known as “biocides”, which means spoiler of living organisms responsible for MIC. Biocides are a standard chemical method applied as a MIC mitigation solution, especially in oil and gas industries[105]. The biocides may be single or a group of two or more compounds employed to kill microorganisms or destroy microbial growth. Feasibility of a biocide depends on the properties of microbes to be destroyed and the operating conditions of the material structures. So, it is instructed to do *in vitro* experiment to determine the exact dosages of the biocides suitable for the material systems prior to direct application. The authoritative criteria for a reliable industrial biocide are:

(i) Selective toward microbes to be killed.

(ii) Effective with and without all other compounds present in the working system.

(iii) Cheap.

(iv) Retard corrosion.

(v) Biodegradability.

Biocides interfere with the bacterial existence in order to prevent biofilm formation on the metal surface. So, this method is successful in controlling sulphate reducers. Biocides can be classified into two categories: oxidizing biocides and non-oxidizing biocides[106]. Freshwater systems are the favoured system for oxidizing biocides. Chlorine, bromine and chlorine-containing compounds such as bleach and chlorine dioxide are commonly oxidizing biocides, producing an affordable biocide hypochlorous acid. Hypochlorite is another oxidizing biocide used for drinking water and in oil field waters. Oxidizing biocide is more reactive than non-oxidizing biocides[107].

Non-oxidizing biocides are synthetic molecules that can be employed in various operating systems. They are appreciably financially beneficial in structural materials having reduced hydrocarbon contents[108]. Table 1.4 summarizes some of the non-oxidizing inhibitors.

Table 1.4: Some of the non-oxidizing inhibitors with their advantages and disadvantages

| Non-oxidizing inhibitor | Advantages | Disadvantages |
|---|---|---|
| Formaldehyde | ▪ Financially sound | ▪ Carcinogenic<br>▪ Required large amounts |
| Glutaraldehye | ▪ Relatively not sensitive to sulphide | ▪ Demobilization by amines and oxygen |
| Quaternary amine compounds | ▪ Broad activity<br>▪ Constancy<br>▪ Inertness towards other substances | ▪ Delayed action<br>▪ Foaming |
| Carbamates | ▪ Effective against SRB | ▪ Required large amounts<br>▪ React with metal ions |
| Metronidazole | ▪ Active against SRB<br>▪ Unresponsive to various substances | ▪ Unique for anaerobic microorganisms |
| Isothiazolone | ▪ Broad activity<br>▪ Degradable | ▪ Highly expensive<br>▪ Not applicable to sour medium |

Hsu et al.[109] investigated the antimicrobial activity, and corrosion mitigation power of a non-poisonous biocide, called benzyldimethyldodecylammonium chloride (BDMDAC), against 304 stainless steel corrosion dipped in a *Desulfovibrio desulfuricans* inoculated solution. Environmental rules and regulations about safety concerns on the application of biocides forced to synthesize environmentally-friendly biocides. This compound proved to be a green microbial corrosion inhibitor. Table 1.5 exhibits some of the recently reported synthetic MIC inhibitors.

Wang J. et al.[110] reported that sodium pyrithione functioned as a microbial corrosion inhibitor on carbon steel using weight loss, electrochemical and molecular modelling. Planktonic and sessile SRB were target microbes, and 80% inhibition efficiency was reported. Shaban S. M. et al.[111] studied the MIC inhibition behaviour of alginates polymeric cationic surfactants on mild steel in 1 M HCl by G (+ve) and G (-ve) bacteria and fungi using spectroscopic tools like FTIR and $^1$H NMR, physicochemical, electrochemical and surface morphological studies. They found that these inhibitors behaved as a mixed-type inhibitors.

Table 1.5: Recently reported biocides for inhibiting MIC

| Sl. No. | Metal/Medium/Bacteria | Biocide/Inhibitor |
|---|---|---|
| 1 | Planktonic and sessile SRB on X80 carbon steel | Sodium pyrithione |
| 2 | Mild steel in 1 M HCl by G (+ve) and G (-ve) bacteria and fungi | Alginates polymeric cationic surfactants |
| 3 | SRB | *Polyalhia longifolia* plant |
| 4 | Mixed SRBs culture | ZnO-interlinked chitosan nanoparticles |
| 5 | Sulfate-reducing microorganisms | Zinc pyrithione |
| 6 | Mild steel in cold water by *Bacillus thuringiensis* EN2 | Ginger extract |
| 7 | Sulfidogenic bacteria | Cationic Gemini surfactants |
| 8 | 5.49% NaCl against Sulfidogenic bacteria from oil-field water tank | Cationic Gemini surfactants |
| 9 | Carbon steel in 0.5 M HCl against SRB | Tetra hydroxyl methylphosphonium sulphate with fatty acids |
| 10 | API 5L X80 line pipe steel in artificial seawater by SRB | Neem extract |
| 11 | Carbon steel and stainless steel in oilfield environments by *Bacillus subtilis* A1 and *Streptomyces parvus* B7 | *Allium sativum* |

Vaithiyanathan S. et al.[112] discovered that *Polyalhia longifolia* plant has green corrosion inhibition power against SRB. They confirmed this fact utilizing TEM, SEM, FTIR, potentiodynamic polarization and weight loss studies. Rasool K. et al.[113] reported that mixed SRBs culture isolated from oilfields increased MIC and ZnO-interlinked chitosan nanoparticles mitigated corrosion establishing SEM, TEM, XRD and FTIR monitoring techniques. Carlson H. K. et al.[114] analyzed the MIC of sulfate-reducing microorganisms (SRM) and inhibition using potent biocide zinc pyrithione by highthroughput (HT) approach. Narenkumar J. et al.[115] disclosed a green MIC inhibitor ginger extract to apply for mild steel corrosion. Cooling water was the medium, and *Bacillus thuringiensis* EN2 was the target microbes. Ginger extract showed 80% inhibition efficiency at 20 ppm of ginger extract and, calculated by weight loss, electrochemical, XRD and FTIR techniques. Labena A. et al.[116] studied corrosion inhibition properties of cationic gemini surfactants by sulfidogenic bacteria by employing redox potential and sulphide productivity. It was found that this inhibitor destroyed the biofilm growth at 0.1 mM concentration of surfactants. Labena A. et al.[117] also experimented with the same inhibitor in 5.49% NaCl against sulfidogenic bacteria from an oil-field water tank. They said that 97% corrosion inhibition power at 5 mM inhibitor concentration conducting sulphide production, redox potential and corrosion inhibition studies. Aiad I. A. and coworkers[118] proved MIC inhibition power of Tetra hydroxylmethylphosphonium sulphate with fatty acids on carbon steel in 0.5 M HCl by SRB employing FTIR, $^1$H NMR, surface tension, critical micelle, weight loss and electrochemical methods. The inhibition effect of Neem extracts on the MIC of API 5L X80 line pipe steel by a sulphate-reducing bacterial (SRB) consortium was recommended by Shaily M. Bhola and team[119]. They carried out FESEM coupled with EDS and electrochemical studies to establish a 50% reduction power of MIC rate. Punniyakotti Parthipan and coworkers[120] suggested that *Allium sativum* as a green MIC inhibitor on carbon steel and stainless steel in oilfield environments in the presence of *Bacillus subtilis* A1 and *Streptomyces parvus* B7 by conducting weight loss and electrochemical techniques.

Schiff bases are synthetic organic compounds with potent activities in various disciplines such as medicine, agriculture and cosmetic products. Many Schiff bases exhibit anticancer, antitumor, antibacterial etc., properties. Schiff bases are popular compounds for synthesizing numerous antibacterial drugs due to their fast and straightforward synthetic methods and their tendency to coordinate with their functional groups. Some recently reported Schiff bases as MIC inhibitors for metal surfaces in various environments in the presence of microorganisms mentioned below.

Nabel A. Negm et al.[121] synthesized four active Schiff base surfactants (Fig. 1.17a) derived from ketoglutaric acid and fatty alcohol as corrosion inhibitors with the properties of SRB biocide. They confirmed the inhibition efficiency of synthesized Schiff bases using weight loss studies. The surface properties of the Schiff bases were estimated using surface tension-log concentration profiles.

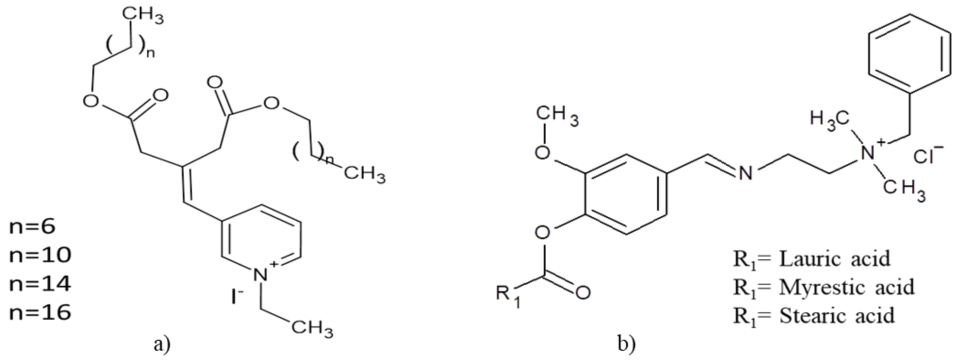


Fig. 1.17: Structure of a) quaternary ammonium Schiff base-alkyl ketoglutarate b) Schiff base derived from vanillin

Atef S. K. and coworkers[122] prepared three Schiff base surfactants (Fig. 1.17b) derived from vanillin and fatty acids and characterized them using FTIR and $^1$H-NMR techniques. A mixed culture of SRB isolated from an oil field tank was targeted to prove the antimicrobial effect of the newly synthesized Schiff bases. They concluded that Schiff base cationic surfactants were suitable MIC inhibitors for industrial applications.

Samy M. Shaban and coworkers[123] reported three Schiff base cationic surfactants (Fig.1.18) derived from 4-dimethylaminobenzaldehyde and monoethanolamine acted as MIC inhibitors for carbon steel in acid medium against SRB. They applied physicochemical and electrochemical studies to confirm the inhibition behaviour of the synthesized Schiff bases.

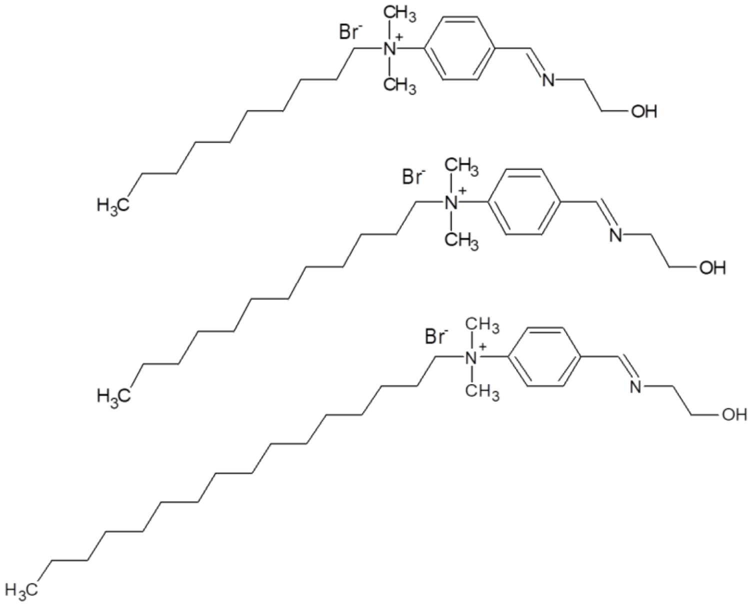


Fig. 1.18: Structures of three Schiff bases derived from 4-dimethylaminobenzaldehyde

Nabel A. Negm et al.[124] carried out a synthetic procedure for a series of Schiff base cationic surfactants (Fig.1.19) and their transition metal complexes by condensation reaction between fatty amines and 4-diethyl aminobenzaldehyde to study the biocidal activity of these compounds against SRB.

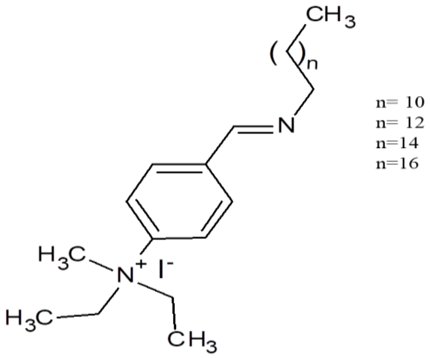


Fig. 1.19: Structure of Schiff base derived from 4-diethyl aminobenzaldehyde

It was reported that parent Schiff bases and their metal complexes showed remarkable biocidal activity.

Various recognition and effective approaches are being developed to fight MIC, yet more advancement is essential. Numerous problems want to be identified and addressed by using new technologies that will regulate MIC. Application of environmental friendly biocides/inhibitors to substitute other harmful inhibitors will be cost effective and eco-friendly. Predominant issue that have to be studied in future is associated to the selection of methodologies. More deep knowledge of mechanisms related to every MIC inhibitory process could likewise be a significant area of future research.

## Scope and objectives of the present investigation

Natural plant products are a source of myriads organic compounds having the potential to donate lone pair of electrons from the compounds to the metal surface. Hence, plant products can function as effective corrosion inhibitors. Many researchers were investigated natural plant products like leaf, seed, root, fruit, flower etc., as an efficient, eco-friendly corrosion inhibitor on the mild steel surface in aggressive acid environments.

The present research concentrates on extracting seven different natural plant products such as *Ixora coccinea* extract (ICE), *Croton persimilis* extract (CPE), *Tinospora cordifolia* extract (TCE), *Garcinia cambogia* extract (GCE), *Clerodendrum infortunatum* extract (CILE and CIRE) and *Dioscorea bulbifera* extract (DBE) and monitoring them as corrosion inhibitors for mild steel in 1 M HCl and 0.5 M $H_2SO_4$ media. FTIR and UV-Visible spectroscopy are used to characterise functional groups in extracts and determine the metal-binding ability of the extracts, respectively. Weight loss measurements, electrochemical studies such as EIS, potentiodynamic polarization and noise measurements are proposed to investigate the corrosion inhibition efficiency of extracts. Surface characterisations are carried out using SEM and AFM. It is also suggested to clear the mechanism of corrosion inhibition by evaluating various adsorption isotherm models. The impact of temperature on corrosion mitigation efficiency is examined, and deriving thermodynamic parameters of activation like enthalpy, entropy and energy. Quantum mechanical calculations are also recommended to achieve energies of HOMO, LUMO and other quantum mechanical parameters. The impact of temperature, extract concentration and acid concentration on inhibition efficacy is also analysed by statistical tools like response surface methodology and Box-Behnken Design/Central Composite Design.

Schiff bases have a significant role in industrial, catalytic and pharmaceutical fields due to their adaptability and simple synthetic preparations. They have functional groups containing hetero atoms, unsaturated bonds can donate lone pair of electrons and function as potential corrosion inhibitors. Many synthetic compounds like Schiff bases, quaternary ammonium compounds, heterocyclic compounds etc. and natural plant extracts were reported as microbial induced corrosion inhibitors for microorganisms on the metal surfaces in various media. However, the literature survey exhibited that Schiff bases derived from heterocyclic compounds like acetyl pyridine and pyridine carbaldehydes were not investigated as MIC inhibitors.

Herein, previously reported four Schiff bases derived from 2-acetylpyridine, pyridine 2-carbaldehyde and pyridine 3-carbaldehyde such as N-hydroxy-1-(pyridin-2-yl) methanimine (NHP2M), N-hydroxy-1-(pyridin-3-yl) methanimine (NHP3M), (E)-2-(1-(2-phenylhydrazono) ethyl)pyridine (2PHEP) and (E)-2-(1-triazylidineethyl) pyridine (2TAEP) are employed as microbial induced corrosion inhibitors against microorganisms isolated from seawater on mild steel. Various corrosion monitoring techniques like weight loss measurements, electrochemical studies such as EIS, potentiodynamic polarization techniques are also presented to determine the MIC mitigation efficiency of these compounds. The changes observed in the metal surface are examined using optical micrographs of the metal surfaces. The mechanism of MIC inhibition is determined by surface analysis such as XRD and FTIR of corrosion products. The affinity of Schiff base inhibitor towards metal surface confirmed by taking UV-Visible spectra of inhibitor and ferric salt solutions individually and combined. Antibacterial effects of Schiff base inhibitors were studied to verify the inhibition mechanism.