CHAPTER-II

LITERATURE SURVEY & SCOPE OF THE PRESENT INVESTIGATION

2.1 LITERATURE SURVEY

The importance of corrosion is of three fields. The first area of significance is economic, second is improved safety and the third is the prime motive for much of the current research in corrosion. The economic losses are divided into direct losses and indirect losses.

Infact, the impact of corrosion mitigation on our economy would be drastic. For example automobiles, ships, underground pipelines and household appliances would not require coatings. Most metallic plants, as well as consumer products, would be made of steel or cast iron. Corrosion touches all inside the home, on the road, on the sea by corroding the ship materials, in plant and in aerospace vehicles. From the stand point of nation’s economy, the logic underlying the importance of corrosion studies are manifold. For metals forming under present day complex and variable service conditions, controlling corrosion by isolated developments and treatments are essential.

Millions of dollars are lost due to corrosion and much of this loss is due the corrosion of iron and steel, although many other metals may corrode as well. Therefore the corrosion should be controlled or any preventive measures should be taken in order to minimize corrosion.

Abundance of literature are available on the corrosion and its control of mild steel in various industrial processes. Some recent articles discuss about the corrosion inhibitors of mild steel by using some organic inhibitors and natural products.
The use of inhibitors is one of the most practical methods for protection against corrosion in acidic media [148]. HCl and H₂SO₄ are generally initiated as acidic media in the corrosion study of ferrous alloys. Most commercial inhibitor formulations include aldehyde and amines in their structure [149]. On the other hand most well known acid inhibitors are organic compounds that contain N, S or O atoms [150,151]. Several Schiff bases have recently been investigated as corrosion inhibitors for various metals and alloys in acid media [152,153]. Due to the presence of the acetyl group in the molecule, Schiff bases behave as good corrosion inhibitors. Besides the imine group, substitution of different elements also affects the inhibition properties.

Macrocyclic polyether compounds containing a 1, 3, 4-thiadiazole has emerged recently as a new and potential class of corrosion inhibitors on 1 M HCl solution. A survey of the literature reveals that despite the high ability of macrocyclic compounds to interact strongly with the metal surface, little attention has been made on use of these compounds as corrosion inhibitors [91–94].

Availability of nonbonded-(lone pair) and p-electrons in alkenes, alkynes and aromatic rings in inhibitor molecules may involve in chemisorption. The strength of the coordinate covalent bond thus formed depends upon the electron density and polarizability of the donor atom of the functional group [95]. It has also been proposed that the alkynes undergo polymerization to form a protective film on the metal surface [96] and the film prevents mass transport and results in inhibition of corrosion [97]. There are not many organic inhibitors, which are equally effective against corrosion attack on mild steel in HCl as well as H₂SO₄ media. In a recent study [98] it has been found that a group of oxadiazoles are very good inhibitors of corrosion of mild steel in 1 M HCl, having an inhibition efficiency (IE %) greater than in 1 M Sulphuric acid. The Schiff bases of
cinnamaldehyde and p-anisidine gave much better inhibition effect [99] in 1 M HCl than
in 1 M H₂SO₄ at elevated temperature.

Different groups of organic compounds have been reported to exert inhibitive
effects on the corrosion of mild steel. The inhibitive action of various indoles, azoles,
triazoles and a quaternary ammonium salts having surfactant properties on the corrosion
of mild steel in Sulphuric acid media has also been reported [100]. It is the functional
group in the organic molecules that render important services in the inhibition of
corrosion; inhibitory actions of a plethora of functional groups are described in the
literature [101-104]. Isoxazolidines, extensively used in the synthesis of various natural
products of biological interest, are known for many decades. However, only recently, the
isoxazolidine functionality has been introduced to the corrosion inhibition of mild steel
[105].

Compounds containing both nitrogen and sulphur groups generally give rise to
satisfying inhibitor efficiency in the case of iron corrosion in HCl medium [106, 107].
However, data regarding the use of N-heterocyclic compounds like thiadiazole derivatives
are not so plentiful. Azhar et al., have reported in a recent study about the relationships
between the n-pyridyl substituted thiazidazoles reactivity and their ability to inhibit the
corrosion of mild steel in acidic media [108, 109].

The ability of the n-pyridyl thiaadzole molecule to chemisorb on the steel surface
varies with the position of the nitrogen atom in the pyridyl substituent. Using the semi-
empirical quantitative structure activity relationships approach, they have also established
a direct significant correlation, for isomers of n-pyridyl substituted thiaadzoles, between
their molecular structure and their inhibition efficiency. In continuation of the work on
acid corrosion inhibition by thiaadzoles derivatives, they have reported the evaluation of

43
this new class of thia Diazoles \([3,5\text{-bis}(2\text{-thienyl})-1,3,4\text{-thiadiazole} \text{ and } 3,5\text{-bis}(3\text{-thienyl})-1,3,4\text{-thiadiazole})\), taken as inhibitor models of mild steel corrosion in acid medium.

Most of the well known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms. The influence of organic compounds containing nitrogen such as amines and heterocyclic compounds on the corrosion of steel in acidic solutions has been investigated by several researchers [110, 111]. The existing data showed that most organic inhibitors act by adsorption on the metal surface. This phenomenon is influenced by the nature and surface charge of metal by the type of aggressive electrolyte and by the chemical structure of inhibitors [112].

A perusal of the literature on acid corrosion inhibitors reveals that most organic substance employed as corrosion inhibitors act by adsorption on the metal surface. The adsorption mainly depends on the presence of p-electrons and heteroatoms, which induce greater adsorption of the inhibitor molecules onto the surface of mild steel [113–114]. The compounds containing both nitrogen and sulphur can provide excellent inhibition compared with compounds containing only nitrogen or sulphur [115]. In recent years, \(N\) and \(S\) containing triazole derivatives have attracted much attention owing to their excellent corrosion inhibition performance [116]. Not only can some \(N\) and \(S\) containing triazole compounds give very high values of inhibition efficiency, but they can bring down the hydrogen permeation current to a considerable extent [117]. In contrast to most commercial acid corrosion inhibitors which are highly toxic, many \(N\) and \(S\) containing triazole derivatives are environmentally friendly corrosion inhibitors [118].

Data in the literature show that most organic inhibitors adsorb on metals by displacing water molecules on the surface and forming a compact barrier film [119-121]. One of the most effective ways to judge whether the nature of interaction is physisorption
or chemisorption is to calculate the thermodynamic parameters for the adsorption process. Recently, quantitative structure activity relationship (QSAR) has been a subject of intense interest in many disciplines of chemistry. The developments of semi-empirical quantum chemical calculations emphasize the scientific approaches involved in the selection of inhibitors by correlating the experimental data with quantum-chemical properties. The highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), charges on reactive centre, dipole moment (m) and conformations of molecules have been used to achieve the appropriate correlations.

The effectiveness of an organic substance as an inhibitor depends on the structure of the inhibitor [122]. Raicheva et al., have studied and reported that the variation in inhibitive efficiency mainly depends on the type and the nature of the substitutents present in the inhibitor molecule [123-136]. The inhibitor molecule should have centers capable of forming bonds with the metal surface by electron transfer, in which the metal acts as an electrophile and the inhibitor acts as a Lewis base whose nucleophilic centers are O and/or N atoms with free electronic pairs which are readily available for sharing.

Generally, selections of these inhibitors have been based on an empirical approach. Many attempts have been made to correlate inhibition efficiency with properties of the organic molecules such as geometrical dimension [137], cross-sectional area [138], electron density on the basic nitrogen atom of heterocyclic compound [138], π-bonding between heteroatom and metal ionization potential [139], electron affinity negative logarithm of the ionization constant of the base, pKa , steric effects, molecular structure, Hammett substituent constants, dipole moments and intermolecular forces [140-142]. Quantitative Structure Activity Relationship (QSAR) has been derived for various sets of corrosion inhibitors [143-146], which attempts to find consistent relationship between the
variations in the values of molecular properties and the inhibitor activity for a series of compounds. Khaled et al., have reported the correlation of the molecular fragments with inhibitor performance [147]. Attempts have been made to predict corrosion inhibition efficiency with a number of individual parameters obtained via various quantum chemical calculation methods as a tool for studying corrosion inhibitors.

Acidization of oil and gas wells is probably the most widely used work over and stimulation practice in oil industry [154]. Acidization is an oil reservoir stimulation technique for increasing well productivity. Different acids are used in conventional acidization treatment. The most common are Hydrochloric acid, hydrofluoric acid, acetic acid, formic acid, sulfamic acid and chloro acetic acid. Choice of the acid for a given situation depends on the underground reservoir characteristics and specific intention of the treatment. Migahed et al., [155-159] have investigated the use of HCl for stimulating carbonate-based reservoirs like lime stone and dolomite, HCl is found to act as strong aggressive medium for oil and gas well equipment. Many authors [160-165] have studied the use of organic compounds containing oxygen, sulfur and nitrogen to reduce corrosion attack on steel.

Generally, the use of organic inhibitors to control the metal dissolution is one of the common techniques and during the past decade many inhibitors have been studied in different media [166-172]. Tang et al., [167] have studied the inhibition process of organic compounds such as amines, acetylenic alcohols and they proposed that the adsorption of inhibitor molecule onto the metal substrate is the initial step in the inhibition process. Bentiss et al., [169] have investigated the role of heterocyclic compounds as organic inhibitors which possess at least one functional group. They have considered that the functional group as the reaction centre for the adsorption process. Popova et al.,
[170,171] investigated that the adsorption of an inhibitor is related to the presence of hetero atoms such as nitrogen, oxygen, phosphorus and sulphur as well as a triple bond or an aromatic ring in their molecular structure.

Synergism has become a very important effect in corrosion inhibition processes and serves as the basis for most modern inhibitor formulations. The increase in inhibition efficiency of organic compounds in the presence of some ions has been reported by some authors and was ascribed to the synergistic effect [173-175]. Kalman et al., [176] have reported that the synergistic effect increases the inhibition efficiency of hydroxyl-ethane-1,1-diphosphonic acid in the presence of divalent cations such as Zn$^{2+}$. Rajendran et al., [177] have also observed the synergistic effect of calcium gluconate and Zn$^{2+}$. Similar effects have been observed in the presence of some anions, particularly halide ions. Gomma [178] studied the effect of halide ions on the inhibition efficiency of pyrazole derivatives and observed that the synergistic effect increased in the order $\text{Cl}^− < \text{Br}^− < \Gamma^−$. Oguzie [179] reported similar observation for the influence of halide ions on the inhibitive action of some organic dyes. Zhang et al., [180] reported the synergistic effect of iodide ions on the efficiency of Benzotriazole. El-Hosary and Saleh [181] have also reported the synergistic effect of iodide ions on the inhibition efficiency of molasses. It is thought that the initial specific adsorption of the halide ions on the metal surface improves adsorption of the organic cations in acidic solution by forming intermediate bridges between the positively charged metal surface and the positive end of the organic inhibitor.

Corrosion inhibition by synergism thus results from the increased surface coverage arising from ion-pair interactions between the organic cations and the anions. Recently, due to increasing environmental awareness and the need to develop environmentally friendly processes, attention has been focused on the corrosion inhibiting properties of
natural products of plant origin. This area of research is of much importance because in addition to being environmentally friendly and ecologically acceptable, plant products are inexpensive, readily available and renewable sources of materials. Zucchi and Omar [173] have studied a variety of plant extracts and reported that Auföpio turkiae and Azydracta indica reduced the corrosion of mild steel in 1M HCl with a good efficiency. Saleh et al., [180] have reported that aloe leaves and peels from mangoes and oranges gave adequate protection to mild steel in Hydrochloric acid solutions. Quraishi [182] have even observed possible synergism of hydroxyl-ethane-1,1-diphosphonic acid HPED with some plant extracts.

Aniline compounds have also been found to be effective inhibitors for mild steel in HCl [183]. These compounds can absorb on the metal surface, block the active sites and thereby reduce corrosion rate. Quaraishi et al., [184,185] have studied the inhibition characteristics of some condensation products and aromatic hydrazides in HCl. Corrosion inhibition of steel with some Schiff base compounds in HCl have also been reported by some other researchers [186,187]. They observed that most of heterocyclic compounds containing nitrogen, sulphur or oxygen and the sites of these elements are considered as chemisorption centers. These elements possess higher electron density and are called as electroactive groups. The electron density on these centers is the direct measure of inhibition efficiency of the inhibitor [188,189].

In order to reduce the corrosive action in aggressive environment, the inhibitory nature of many organic compounds containing heteroatoms like N, S and O which have high basicity and electron density has been studied. Many heterocyclic compounds such as triazoles, quinoline and pyridine were evaluated for their corrosion inhibition nature. Natural products like lignin, tannin, cinchona alkaloids and pomegranate alkaloids [191]
have been evaluated as very effective acid corrosion inhibitors in standard as well as in stringent conditions. The corrosion inhibition of mild steel have also been studied with the extracts of Antrographis paniculata [190], Thespesia populnea, Mangifera indica [192], Datura metal, Mentha pulgeium [193], Sesbania grandiflora seeds [194], Ficus benghalensis bark [195], Psidium gerajanra (bark) and Callistemos (leaves) [196], Canavalia ensiformisp [197] etc. The studied natural inhibitors have been found to be highly eco-friendly and possess no threat to the environment.

Literature shows a growing trend in the use of natural products known as non-toxic compounds, also called as green corrosion inhibitors. We have cited literatures concerning natural honey, nypa fructicans wurmb [198], opuntia extract [199], saccharides [200], natural tannins extracted from acacia and from pine bark [201], tryptamine [202] as effective environmental friendly corrosion inhibitors. Natural plants are added as extract, oil or pure compounds and are the subject of various contributions: limonene [203], ginger [204], henna [205], jojoba oil [206], rosemary oil [207], artemisia oil [208], bgugaine [209-211], thym [212], eugenol and acetylenic [213], pulegone [214], menthols [215], cedar [216], rosmarinus [217], pulegone [218-220], have been found to be very efficient corrosion inhibitors for metal in aggressive media.

Sanyal [221] in his review has given a vivid account of organic corrosion inhibitors including the classification and mechanism of action. He has reported that the attribution of corrosion inhibition of mild steel by the donation of lone pair of electron to metal atoms. A number of heterocyclic compounds [222-225] have been reported as corrosion inhibitors and the screening of synthetic heterocyclic compounds is still being continued. Though many synthetic compounds showed good anticorrosive activity, most of them are highly toxic to both human beings and environment. The safety and
environmental issues of corrosion inhibitors arose in industries has always been a global concern. These inhibitors may cause reversible (temporary) or irreversible (permanent) damage to organ system viz., kidneys, liver or to disturb a biochemical process or to disturb an enzyme system at some site in the body. The toxicity may manifest either during the synthesis of the compound or during its applications. These toxic effects have led to the use of natural products as anticorrosion agents which are eco-friendly and harmless. In recent days many alternative eco-friendly corrosion inhibitors have been developed, they range from rare earth elements [226-228] to organic compounds [229-232].

Generally the effect of some inorganic anions on the corrosion of tin in Citric acid solution was also studied [233]. Citric acid is the natural organic acid produced in oranges and other citric fruits. It is generally regarded as safe for use in food products. It is a common material used in many food and beverages, including most of the carbonated beverages sold on the market. This means that Citric acid is compatible with the environment and can usually be blended into sanitary sewage systems with environmental agency approval. Hammouti et al., have studied the feasibility of application of non-toxic compounds like aminoacids and aminoesters and their derivatives as good inhibitors in various corrosive solutions [234–240]. They proved that the methionine ethyl ester as efficient inhibitor for pure iron in Citric acid solutions [241] and they have analyzed some aminoacid compounds.

S.S. Abdel Rehim et al., [242] have investigated the corrosion of tin in Citric acid solutions by potentiodynamic and cyclic voltammetric techniques. Moreover, the effects of the inorganic anions CrO$_4^{2-}$ (toxic), MoO$_4^{2-}$, NO$_3^-$ and NO$_2^-$ on the corrosion behaviour of tin in this carboxylic acid have been investigated.
2.2. SCOPE OF THE PRESENT INVESTIGATION

In a modern business environment, successful enterprises cannot tolerate major corrosion failures, especially those involving personal injuries, fatalities, unscheduled shutdowns and environmental contamination. For this reason, considerable efforts are generally employed in corrosion control at the operational phase. Corrosion can lead to failures in plant infrastructure and machines which are usually costly to repair, costly in terms of lost or contaminated product, in terms of environmental damage and possibly costly in terms of human safety.

Corrosion is an inevitable foe that should be accepted as an inevitable process. Actually, something can and should be done to prolong the life of metallic structures and components exposed to the corrosive environments [243].

There are different types of methods such as cathodic protection [244], anodic protection [245] and materials such as organic (polymeric) and metallic coatings [246-255] and use of chemical inhibitors [256-258] available for protecting corrosion of metals and alloys. Among the different types of methods, the use of inhibitors is one of the most practical methods for protection against corrosion in acidic media. However, nearly all powerful corrosion inhibitors may have detrimental effects on both environment and health due to their toxic and carcinogenic nature. Therefore, there is a need for a primer that provides an excellent inhibition, low cost, and is environmentally safer.

Mild steel is a widely used in most of the chemical industries, construction purposes in building of house and in construction of ship. This is due to its low cost and easy availability for fabrication of various products etc. Since it suffers from severe corrosion in aggressive environments like air and water, the metal has to be protected.
Acids have been used for drilling operations, pickling baths and in de-scaling processes. To reduce the corrosion problems in these environments, inhibitive effects of various organic compounds have been tried so far.

Organic compounds having hetero atoms are found to have higher basicity and electron density and thus assist in corrosion inhibition. There are numerous naturally occurring substances like Embellica officinalis, Terminalia chebula, Terminalia bellirica, a mixture of latter three, Sapindus trifolianus, Acacia concianna, Swertia aungustifolia and Quinoline based Cinchona alkaloids, Eucalyptus leaves and Eugenia jambolans that have been evaluated as effective corrosion inhibitors.

Due to the bio-degradability, eco-friendliness, cost-effectiveness, less toxicity and easy availability of these materials, the trend of using them have become increasingly important in the recent years.

Therefore in this investigation, the corrosion of mild steel used in the construction purpose has been studied in absence and presence of various natural and organic inhibitors. These inhibitors were assessed by weight loss method and the obtained results were further confirmed by the electrochemical techniques such as open circuit potential, polarization and electrochemical impedance.
2.3. OBJECTIVES OF THE PRESENT INVESTIGATION

The present investigation has been focused on synthesis and use the inhibitive role of three different corrosion inhibitors namely Benzotriazole, Piper nigrum.L and Adhatoda vasica. The study was carried out with the following objectives;

A to synthesize environmental friendly Benzotriazole organic base for the effective inhibition of mild steel corrosion.

A to extract and prepare Piper nigrum.L and Adhatoda vasica (AV) as natural inhibitor for mild steel corrosion.

A to ascertain the structure of the synthesized formazan derivatives by FT-IR and NMR studies.

A to study and explore the possibility of utilizing the synthesized compounds as alternatives to toxic inhibitor for corrosion inhibition of mild steel.

A to investigate and optimize the inhibitive behavior of synthesized inhibitors and natural product inhibitor by weight loss measurement.

A to study the nature of adsorption and surface coverage by verifying various adsorption isotherm.

A to analyze the inhibitive role of studied inhibitor by Open Circuit Potential (OCP) potentiodynamic polarization (Tafel) and electrochemical impedance studies.

A to characterize the nature and morphology of the inhibited mild steel by Fourier Transform Infrared Spectra (FT-IR) and Scanning Electron Microscopy (SEM) studies.

With these objectives, a search for new effective and environmentally friendly corrosion inhibitors was successfully performed and developed in order to address the possibility of utilizing them for mild steel in various aggressive environments.
2.4 WORK-PLAN

Corrosion behaviour on mild steel using inhibitors

Organic base inhibitor (Benzotriazole)

&

Extraction of inhibitor (Piper nigrum.L, AV)

Weight loss method

Electrochemical method

Adsorption study

Surface analysis

Open Circuit Potential

Polarization Tafel

Electron Impedance Spectroscopy

SEM FT-IR