CHAPTER 2

STATE OF THE ART AND SCOPE OF INVESTIGATION

2.1 STATE OF THE ART

Most industries depend heavily on the use of metals and alloys. One of the most challenging and difficult tasks for industries is the protection of metals against corrosion. Corrosion is a serious problem that continues to be of great relevance in a wide range of industrial applications and products; it results in the degradation and eventual failure of components and systems both in the processing and manufacturing industries and also in the service life of many components. Corrosion control of metals and alloys is an expensive process and industries spend huge amounts towards this problem. Mild steel is widely applied as the constructional material in many industries due to its excellent mechanical properties and low cost. The damage of mild steel by corrosion results in high cost towards maintenance and protection of materials used.

Corrosion is the deterioration of metals / alloys by chemical interaction with their environment. Millions of dollars are lost every year because of corrosion. Much of this loss is due to the corrosion of iron and steel although many other metals may corrode as well. Corrosion damage can cause leakage of fluids or gases. Even more dangerous effect is the loss of strength of the structure induced by corrosion and subsequent failure. The application of acid corrosion inhibitors in the industry is lies initially in the prevention or minimization of material loss during contact with acid
The electrochemical corrosion is generally caused by asymmetry in the potentials between metal and strong acid. The aggressivity of hydrogen ion is inevitable in uninhibited acid. Protons and dissolved oxygen are termed as natural motors of corrosion (Abdallah et al. 2009, Abdallah et al. 2012). Facing this problem, the corrosion inhibitors are required. Works on the inhibition are too exhaustive to be quoted. But scientists are unanimous on the fact that the protection of metals by which is provided by the adsorption of inhibitors on the metal surface (Rupesh Kushwah & Pathak 2014).

Acid solutions are widely used in several industrial processes, such as acid pickling of steel, chemical cleaning and processing, ore reduction/metal extraction and oil well acidification. Because of the general aggression of acid solutions, inhibitors are commonly used to reduce the corrosive attack on metallic materials. The selection of inhibitor is controlled by its economy, efficiency to inhibit the substrate material and environmental toxic effects. Most of the excellent acid inhibitors for corrosion of steel in acidic medium are organic compounds containing nitrogen, oxygen and/or sulphur atoms (Sobhi et al. 2012). According to Hackerman coworker (Annand et al. 1965), the inhibiting properties of many compounds are determined by the electron density at the reaction center. With an increase in the electron density at the reaction center, the chemisorbed linkage between the inhibitor and the metal are strengthened. Hackerman established a mechanism for the protective properties of pyridine and its derivatives.

Corrosion is the gradual destruction of materials usually by chemical reaction with its environment. The corrosion is severe due to the presence of Cl\textsuperscript{−} ions and dissolved oxygen. Water has been used as cooling fluid in various industries. Mild steel is widely used as infrastructure material in marine environments (Satyanarayana et al. 2012, Baker et al. 2011,
Durodola et al 2011). It is one of the major constituents in structural steel applications including body of a ship, offshore platforms, foundation pilling, sheet pilling and coastal facilities. It is also used in industry where the metal is exposed to acid corrosion. So it is imperative to study the corrosion aspect and find out suitable corrosion inhibitors to be used with aqueous / acid medium. Inhibition of corrosion and salting can be done by the applications of inhibitors which is one of the most practical and economic methods for protection against metallic corrosion (Zou et al 2011, Khaled & Hackerman 2003, Ali et al 2003). 1-(8-Hydroxyquinolin-2yl-methyl)thiourea has been used as a corrosion inhibitor in controlling corrosion of mild steel immersed in aqueous solution containing 60ppm of Cl’ (Syed et al 2013).

Azo compounds are the most widely used class of dyes due to their application in various fields, such as the dyeing of textiles and fibres (Abdalalah & Moustafa 2004). Some studies have shown that the inhibition of the corrosion by organic dyes is mainly attributed to the formation of complex compounds between the metal-ions and the nitrogen of azo binding at the electrode surface (Ebenso et al 2008, Hanan et al 2014). The oleyl-amido derivatives provide a good protection to steel against pitting corrosion by shifting the pitting potential towards the noble direction (Zaafarany 2013). Benzoic acid and substituted benzoic acids are widely used as corrosion inhibitors(Akiyama & Nobe 1970).

Adsorption and inhibitor efficiencies of benzoic acids depend on the nature of the substituents. Electron donating substituents increase inhibition by increasing the electron density of the anchoring group (-COOH group); on the other hand, electron-withdrawing, substituents decrease inhibition by decreasing the electron density. Benzotriazole (BTA) and its derivatives are effective inhibitors for many metals, especially copper, in a variety of conditions (Fox 1979). At low concentrations, BTA is adsorbed slightly on
the surface. At sufficiently high solution concentrations, bulk precipitation of the complex on the surface occurs, inhibiting corrosion. Formation of this complex is a slow process and, as a result, the inhibitor efficiency of BTA increases with time. Thiourea and its derivatives are used as corrosion inhibitors for a variety of metals (Singh 1993). They are nontoxic and are not an environmental hazard. The variation in the inhibitor efficiencies of various derivatives of thiourea depends on the molecular weight. By using lower concentrations of large molecules, higher inhibitor efficiencies.

Most of the inhibitors used in cooling water nowadays are based on phosphonates, either alone or in combination with one or more other corrosion inhibitors. Phosphonates give better inhibition efficiencies when used in combination with zinc salts. Bohnsock et al. have also studied the inhibition action of 2-phosphonobutane 1,2,4-tricarboxylic acid on carbon steel at room temperature and a pH range of 6.5–8. They have found that the addition of phosphonocarboxylic acids to water has a considerable effect in preventing corrosion as well as scale formation in water recirculating systems. Moreover, the efficiency of phosphonocarboxylic acids as corrosion inhibitors has been found to improve by the addition of zinc salts and/or phosphoric acid. In spite of the advantage of combining zinc salts with certain inhibitors like the phosphonates, they have been found to adversely affect the water released during the cooling process. Therefore, the permissible limit of zinc in water/wastewater has been restricted to a maximum value of 2ppm (Eswaran & Mathur 1996). As a result of the adverse effects of the salts of the heavy metals, researchers have decided to employ effective corrosion inhibiting compositions that are free from metal ions. Such types of inhibitors are highly necessary in industry for the protection of metallic equipments.

During acidizing stimulation or cleanup operations, metal tubulars, down hole tools/valves, surface lines, etc. are exposed to acidic fluids and are
prone to corrosion. Because corrosion rates drastically increase in high temperature wells, controlling corrosion is critical and must be dealt with carefully. In addition, corrosion protection is important for maintaining the integrity and long life of down hole tools installed in a well. Several corrosion inhibitors, such as quaternary ammonium compounds, propargyl alcohol-based compounds, etc., have been effectively used in the industry. However, because of stringent environmental regulations, attention has been focused on the development of new corrosion inhibitors that are environmentally friendly. Food-grade products that are considered "green" chemicals have significant potential as corrosion inhibitors in the oil and gas industry. Chicory has been used as a corrosion inhibitor for high-temperature and strong-acidic conditions.

Chicory is a perennial bush plant available in many parts of the world. The root of the chicory plant can be roasted and ground for use as a coffee substitute or additive. Chicory is environmentally acceptable and, being of plant origin, is widely recognized as biodegradable in nature. It has been found that chicory can provide corrosion protection for alloys, such as N-80, 13CrL80, and 1010 steel, in the presence of either inorganic or organic acids at temperatures up to 121°C. Considering its good performance, low price, and no toxicity issues, chicory has significant potential for acid corrosion-inhibition applications.

Pipelines are the safest and most economical means of transporting oil and gas in offshore and onshore production facilities. Corrosion inhibitors continue to play a significant role in protecting the pipelines from internal corrosion. A number of corrosion inhibitors have been developed with low environmental impact without compromising on their inhibitor efficiency. Recently geographical location specific-regulations for several regions have been implemented. The most prominent of these are the environmental
regulations. Environmentally friendly corrosion inhibitors for mild steel in Synthetic Ocean water has been studied by weight loss method. These natural products were designed for application in Indian oil and gas industry and other environmentally sensitive platforms; exploiting their low toxicity-as medicinal plants and ease of biodegradation as water soluble extracts.

2.2 SCOPE OF PRESENT INVESTIGATION

Corrosion in the modern society is one of the outstanding challenging problems in the industry. Most industrial designs can never be made without taking into consideration the effect of corrosion on the life span of the equipment. Recent industrial catastrophes have it that many industries have lost several billions of dollars as a result of corrosion. Reports around the world have confirmed that some oil companies had their pipeline ruptured due to corrosion and that oil spillages are experienced which no doubt created environmental pollution; in addition, resources are lost in cleaning up this environmental mess, and finally, large-scale ecological damage resulted from corrosion effects. The possibility of occurrence of corrosion in an industrial plant has been posing a lot of concern to petroleum, chemical, and mechanical engineers and chemists. It is now known that corrosion can have some effects on the chemistry of a chosen process, and the product of corrosion can affect reaction and purity of the reaction products.

Control of internal corrosion of carbon steel pipeline can be achieved by the injection of corrosion inhibitors. Corrosion inhibitors are surface active compounds that, in small quantities (ppm level), cause a reduction in metal loss due to corrosion. Vast majority of corrosion inhibitors are made up of molecules which are composed of separate hydrophilic head and hydrophobic tail entities. It is this combined hydrophilic/hydrophobic nature that causes an inhibitor to partition between oil and water phases in pipe flow (Smith 1999).
Polymeric compounds consist of large molecules, which can be adsorbed on the surface of a certain metal, hence, these polymers can be considered as corrosion inhibitors. For instance, the potentiality of aliphatic polyamines, polyvinylpiperidines and polyvinylpyridines as corrosion inhibitors has been investigated. The effect of polyvinylpyridine as an inhibitor was attributed to the adsorption of this polymer through several points of each of its molecules. Some authors have found that the inhibiting properties of phosphonates are enhanced when they are combined with polymers. The method for preventing corrosion in water-carrying systems by adding one of the phosphonocarboxylic acids or their salts and other synergistically active substances has also studied. They have found that enhanced inhibition action of phosphonocarboxylic acid can be achieved by adding one of the following derivatives: a benzimidazole derivative; polyacrylamide; polyethyleneimine; or lignin sulfonate. These inhibitors were found to be highly effective in preventing the corrosion of carbon steel in water-carrying systems (Abdalla Abulkibash et al 2008).

2.3 SELECTION OF INHIBITORS

Steel is a ferrous alloy whose major component is iron, with carbon content between 0.02% and 1.7% by weight. Carbon is the most cost effective alloying material for iron, but many other alloying elements are also used. Carbon and other elements act as a hardening agent, preventing dislocations in the iron atom crystal lattice from sliding past one another. Varying the amount of alloying elements and their distribution in the steel controls qualities such as the hardness, elasticity, ductility, and tensile strength of the resulting steel. Steel with increased carbon content can be made harder and stronger than iron, but is also more brittle. The maximum solubility of carbon in iron is 1.7% by weight, occurring at 1130°C; higher concentrations of carbon or lower temperatures will produce cementite which will reduce the
strength of steel. Alloys with higher carbon content than this are known as cast iron because of their lower melting point. Steel is also to be distinguished from wrought iron with little or no carbon, usually less than 0.035%. It is common today to talk about 'the iron and steel industry' as if it were a single entity; it is today, but historically they were separate products. Steel is often classified by its carbon content: a high-carbon steel is serviceable for dies and cutting tools because of its great hardness and brittleness. low- or medium-carbon steel is used for sheeting and structural forms because of its amenability to welding and tooling.

Many organic compounds have been studied to investigate their corrosion inhibition potential, e.g., the effect of organic nitrogen compounds on the corrosion behavior of iron and steel in acidic solutions; these organic nitrogen compounds are usually employed for their rapid action (Behpour et al 2009). Organic inhibitors can adsorb onto the metal/solution interface via four distinct mechanisms: (a) electrostatic attraction between charged molecules and the metal; (b) interaction between uncharged electron pairs in the molecule and the metal; (c) interaction between π-electrons and the metal and (d) a combination of mechanism (a) and (c) (Shorky et al 1998). Generally, the tendency to form stronger coordination bonds and, as a result, the inhibition efficiency increases according to the following trend:

O < N < S < P. The planarity of molecule and lone pairs of electrons present on N, O and S atoms are important structural features that control the adsorption of these molecules onto the surface of the metal (Yesim et al 2012). Schiff bases are effective inhibitors for the corrosion of steel in acidic media. Recent studies reveal that organic compounds containing polar functions groups would be quite efficient in minimizing the effect of corrosion in addition to heterocyclic compounds containing polar groups and π-electrons (Abdel-Gaber et al 2009, Ahmed et al 2014).
Corrosion Inhibition Efficiency (IE) of organic compounds is connected with their adsorption properties. The effect of the adsorbed inhibitor is to protect the metal from the corrosive medium. A perusal of the literature on acid corrosion inhibitors reveals that most organic substances employed as corrosion inhibitors can adsorb on the metal surface through heteroatoms such as nitrogen, oxygen, sulfur and phosphorus, multiple bonds or aromatic rings block the active sites decreasing the corrosion rate (Dubeya & Singh 2007). The inhibition ability of 4,4-dimethyloxazolidine-2-thione (DMT) for mild steel corrosion in a 1 M HCl solution at 30 °C was studied. The inhibition efficiencies increased with the concentration of DMT. The area containing S atom is most possible site for bonding the mild steel surface by donating electrons to the metal. Adsorption of the inhibitor on the mild steel surface has been found to follow Langmuir adsorption isotherm and the value of the free energy of adsorption $\Delta G^{\circ}_{\text{ads}}$ indicate that the adsorption of DMT molecule is a spontaneous process typical of chemisorptions (Ahmed Musa et al 2010).

As the thiourea molecule contains one sulphur and two nitrogen atoms, thiourea and its derivatives are the likely potential corrosion inhibitors (Shetty et al 2008). Selection of effective corrosion inhibitors is very important for an application in which inhibitors are selected based on what kind of metal or alloy and corrosive environment are used. Effectiveness of the organic inhibitors depends on the extent of adsorption and fraction of surface area covered on metal surface. The inhibitive action of some series of organic compounds containing N and S atom against corrosion of steels in 4 N HCl solution and found that they act as anodic inhibitors. The use of thiourea and phenyl thiourea as inhibitors for the corrosion of ferrite and austenitic stainless steel in sulphuric acid medium has also been studied. The results show that the covering effect of phenylthiourea on the metal surface is better than that of thiourea, and the corrosion rate of stainless steels decreased
more remarkably in solutions with phenylthiourea than in solutions with thiourea (Herle et al 2011).

These compounds can adsorb on the metal surface and block the active surface sites to reduce the corrosion rate. Many synthetic compounds offer good anticorrosive action; but most of them risk being highly toxic to both human beings and environment. They are the rich sources of ingredients which have very high inhibition efficiency. The studies in these later years prove that this kind of inhibitor find more and more attention of researchers identified.

Recent studies show that the inhibitive effect enhances of several nitrogen containing organic compounds for steel in acid solutions. Organic nitrogen compounds specify of the corrosion behavior of iron and steel in acidic solutions are usually employed for their rapid action. The synthesis of new pyrazolic, bipyrazolic and tripyrazole compounds is an easy way to obtain several compounds of which the molecular structures contain several heteroatom’s and several substituent’s. This allowed variation in molecules is to be tested on different interfaces metal/ corrosive solution combinations (Bouklah et al 2013). Some cationic surfactants such as, mono and dicaticionic benzothiazolic quaternary ammonium bromide (Popova et al 2011), Alkyl dimethylisopropylammonium hydroxide (Badawi et al 2010), New Schiff base cationic surfactants (Negm et al 2011), are used as inhibitors for corrosion of steel in acidic solutions. They inhibit the corrosion by the adsorption on the steel surface.

Influence of polyvinyl pyrolidone on corrosion resistance of mild steel simulated concrete pore solution prepared in well water in the absence and presence of Zn$^{2+}$ has been evaluated by weight loss method was reported (Shanthi & Rajendran 2013). The upgrading of inhibition efficiency of organic compounds in the presence of some anions, particularly halide ions,
have been reported by us and other authors and has been ascribed to a synergistic effect. It is thought that the anions are able to improve adsorption of the organic cations in solution by forming intermediate bridges between the metal surface and the positive end of the organic inhibitor. Corrosion inhibition synergism resulting from increased surface coverage, arise from ion-pair interactions between the organic cations and the anions (Obot et al 2011). Inhibition effect of 3-pyridinecarboxaldehyde thiosemicarbazone on the mild steel corrosion in one molar hydrochloric acid has been investigated using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (Khaled et al 2010). Studies on the corrosion of metals / alloys in organic acid media are of industrial importance since most carboxylic acids are used as building blocks in a variety of industrial products such as plastics, fibers, drugs, pharmaceuticals, etc.(Thirumalaikumar & Jegannathan 2011).

Most of the corrosion inhibitors are organic compounds containing sulphur or nitrogen in their chemical constituents. It was found out that this kind of compounds is chemically adsorbed on the metal surface forming barrier for mass and charge transfer and consequently decreasing the rate of corrosion (Deepa Rani & Selvaraj 2014). The inhibition of the corrosion of mild steel in 1 M HCl solution by a new synthesised organic compound, namely 1,1’-(2,2’-(2,2’-oxybis(ethane-2,1-diyi) bis(sulfanediyl) bis(ethane-2,1-diyi) diazepan-2-one, has been studied (Khadiri et al 2014). A perusal of the literature on acid corrosion inhibitors reveals that most organic substances employed as corrosion inhibitors act by adsorption on the metal surface. Over the years, considerable efforts have been deployed to find suitable corrosion inhibitors of organic origin in various corrosive media. In acid media, nitrogen-base materials and their derivatives, sulphur-containing compounds, aldehydes, thioaldehydes, acetylenic compounds, and various alkaloids, for example, papaverine, strychnine, quinine, and nicotine are used as inhibitors.
In neutral media, benzoate, nitrite, chromate, and phosphate act as good inhibitors. Inhibitors decrease or prevent the reaction of the metal with the media (Amitha Rani & Bharathi Bai Basu 2012).

Perusal of literature reveals that many N-heterocyclic compounds such as pyrimidine derivatives (Abd El-Maksoud 2003), triazole derivatives (Hassan et al 2007), tetrazole derivatives (Kertit & Hammouti 1996), pyrazole derivative (Gomma 1998), bipyrazole derivatives (Chetouani et al 2005), indole derivatives (Khaled 2008), pyridazine derivatives (Chetouani et al 2003), benzimidazole derivatives (Wahdan 1997) to mention but a few, have been used for the corrosion inhibition of iron or steel in acidic media. The effectiveness of quinoxaline derivatives (N-heterocyclic compounds) as effective corrosion inhibitors for mild steel in sulphuric acid media has been reported (Obot & Obi-Egbedi 2010) Quinoline (QL) and its derivatives namely quinaldine (QLD) and quinaldic acid (QLDA) were tested as inhibitors for the corrosion of steel in 0.5 M HCl by weight loss method at 30 and 40°C (Ebenso et al 2010). Being economical and ecofriendly, the most common procedure to hinder the progress of corrosion involves the use of inhibitors. Organic molecules containing heteroatoms perform efficiently against corrosion typically by making protective film (Mendes et al 2012) on the metal surface. Imidazole and its derivatives represent a class of environment-friendly inhibitors and have substituted toxic materials containing chromate and arsenic. Copper is a relatively noble potential but its significant corrosion rate (Hong et al 2012) in sea water leads to pipeline damage and causes serious economic disasters. Organic corrosion inhibitors used for copper are usually azoles, amines, and amino acids. High inhibition efficiency of heterocyclic molecules is because of an insoluble physical diffusion (Levin et al 2012) barrier on the (oxidized) metal surface.
Corrosion inhibition of C38 steel in 1 M HCl was investigated in the absence and presence of different concentrations of two imidazodervatives namely, 2-phenylimidazo[1,2-a]pyridine and 2-(m-methoxyphenyl) imidazo[1,2-a]pyrimidine were studied (Ghazoui et al. 2012). The inhibition effect of four synthesized novel bis(aminothiazole) derivatives on the corrosion of carbon steel in 0.5M H$_2$SO$_4$ solution was investigated using galvanostatic, potentiodynamic anodic polarization and weight loss techniques (Abdallah et al. 2014). The adsorption of organic compounds depends mainly on the electronic structure of the molecule and that the inhibition efficiency increases with the increase in the number of aromatic ring. In this context, theoretical chemistry has been used recently to explain the mechanism of corrosion inhibition, such as quantum chemical calculations, which has been proved to be a very powerful tool for studying the mechanism (Abdallah et al. 2014, Fouda et al. 2012, Khaled & Al-Qahtani 2009). The reactivity of an inhibitor is closely linked to its frontier molecular orbitals (MO), including highest occupied molecular orbital, HOMO, and lowest unoccupied molecular orbital, LUMO, and the other parameters such as hardness etc.

The compound carboxy methyl cellulose, has been used as corrosion inhibitor for mild steel in various aqueous environments. The corrosion behavior of carbon steel in presence of carboxymethyl cellulose-1-hydroxyethane-1,1diphosphonic acid has been investigated (Shanthi & Rajendran 2013). Corrosion inhibition effect of 2-[4-(methylthio) phenyl] acethyldrazide (HYD) and 5-[4- (methylthio)benzyl]-4H-1,2,4-triazole-3-thiol (TRD) on zinc in 0.1 M HCl was studied by using mass loss, polarization and electrochemical impedance spectroscopy (Shylesha et al. 2011). Application of small biomolecules such as ascorbic acid (AA) as environmental-friendly, low-cost, readily available corrosion inhibitors of rebar corrosion would be favourable. AA has already been proved as a good
steel corrosion inhibitor in acidic 9,10 and neutral media\textsuperscript{11,12} but no investigations of alkaline media have been done so far. The mechanism of corrosion inhibition was considered to be due to the chemisorption of AA molecules obeying the Langmuir adsorption isotherm (Valek et al 2007). L-Cysteine Methyl Ester Hydrochloride (LCMEH) is indicative of the adsorption of molecules leading to the formation of a protective layer on the surface of copper. Potentiodynamic polarization studies suggested that it is a mixed type inhibitor (Zarrouk et al 2011). A new corrosion inhibitors namely 3,7-dimethylquinoxalin-2(1H)-one (CH\textsubscript{3}-Q=O) and 3,7- dimethylquinoxaline-2(1H)-thione (CH\textsubscript{3}-Q=S) were undertaken and their inhibitive performance towards mild steel corrosion of in 0.5 M sulphuric acid at 20°C has been investigated (Aderdour et al 2012).

Most organic inhibitors act by adsorption on the metal surface. To be effective, an inhibitor must also be able to displace water from the metals surface, to block active corrosion sites and interact with the anodic or cathodic reaction sites, to retard the oxidation and/or reduction of corrosion reaction etc. So, the inhibition efficiency of organic compounds depends on factors such as the structure of the inhibitor, the characteristics of the environment, etc (Fouda et al 2014). The corrosion inhibition characteristics of nitrogen containing amino acid L-tryptophan on mild steel in 0.1 M HCl solution, in the temperature range of 30-50°C, was studied by weight loss and potentiodynamic polarization measurements. L-tryptophan significantly reduces the corrosion rates of mild steel with the maximum inhibition efficiency of 83% at 50°C in presence of inhibitor concentration of 500 ppm (Mobin et al 2011). The following drugs has also been used as good inhibitors for mild steel corrosion in acidic solutions: Ceftriaxone, Cefalexin, Doxycycline, Pheniramine, Fexofenadine, Cefobiprole, Cefuroxime, Cefapirin, Dapsone, Mebendazole, Penicillin G, Penicillin V, Cefadroxil, Ampicillin, Sparfloxacin, Chloramphenicol, Ketoconazole, Methocarbamol,
Orphenadrine, Cefotaxime, Cefazolin etc (Ambrish Singh et al 2012). The corrosion inhibition of mild steel in H₂SO₄ in the presence of methocarbamol has been studied using thermometric and gasometric (hydrogen evolution) methods (Ebenso et al 2009).

The inhibition effect of Dimethylaminobenzylidene acetone (DMABA) on mild steel corrosion in 1M phosphoric acid (H₃PO₄) was investigated (Saratha & Meenakshi 2011). The inhibitive effect of Aspilia africana leaves extract on mild steel corrosion in 1.0 M hydrochloric acid (HCl) has been studied at room temperature and at 60ºC. The leaf extract showed good inhibition efficiency on the corrosion of mild steel with optimum values of 88.1% at room temperature and 91% at 60ºC. The Langmuir and Temkin isotherms were used to analyse the adsorption mechanism of the inhibitor-metal interaction (Isreal et al 2014).

A new corrosion inhibitor, N’-(3,4-dihydroxybenzylidene)-3-{{8-(trifluoromethyl)quinolin-4-yl}thio}propanohydrazide (DHBTPH) was synthesized, characterized and tested as a corrosion inhibitor for mild steel in HCl (1 M, 2 M) and H₂SO₄ (0.5 M, 1 M) solutions. (Ramesh Saliyan & Airody Vasudeva Adhikari 2008).

Dyes have been used to give multi-colour effects to anodized aluminium (Talati & Gandhi 1984). Cyanine dyes have been reported as efficient corrosion inhibitors on metal corroderent systems (Maklouf et al 1995). Green S and erythrosine dyes have been studied as potential inhibitors for mild steel corrosion in HCl (Ita et al 2000). A survey of the literature also reveals that the corrosion on aluminium in amine solutions by some dyes has been reported. The corrosion inhibition of mild steel in 2 M H₂SO₄ using Alizarin yellow GG (AYGG) (an azo dye) in the presence of iodide ions was studied. The inhibitive effect of 4-Aminoantipyrine (4-AAP) on the corrosion of mild steel in 0.5 M H₂SO₄ solution at 303 – 323 K was studied by weight
loss measurement as well as computational techniques. Results obtained show that 4-aminoantipyrine functions as a good inhibitor for the corrosion of mild steel in sulphuric acid solution (Acha et al 2012).

The influence of 2,6-bis-(hydroxy)-pyridine, 2,6-bis-(chloro)-pyridine and diethyl 1,1’-(pyridine-2,6-diyl)bis(5-methyl-1H-pyrazol-2-3-carboxylate on the corrosion of steel in 1 N HCl solution has been studied (Elmsellem et al 2014). Some synthetic organic compounds are non-toxic to the environment, particularly, the pyridine containing compounds. Previously, many synthetic organic compounds such as 2,2’-Dithiobis (3-cyano-4,6-dimethylpyridine) (Morad & Kamal El-Dean 2006), N-decylypyridinium bromide, carboxypyridinium bromide, 3-(4- amino-2-methyl-5-pyrimidyl methyl)-4-methyl thiazolium chloride (Abiola 2006), 1-dodecyl-4-methoxy pyridinium bromide (Migahed 2005), bipyrazolic compounds (Benabdellah et al 2007), 1-([[benzyl-(2-cyano-ethyl)-amino]-methyl]-5- methyl-1H-pyrazole-3-carboxylic acid methyl ester, 1-([[benzyl-(2-cyano-ethyl)-amino]-methyl]-5- methyl-1H-pyrazole-3-carboxylic acid ethyl ester (Herrag et al 2008), 4-Methyl-6-phenyl-tetrahydro pyrimidine-2-thione, 4,6-Diphenyl-tetrahydro pyrimidine-2-thione, 4-Phenyl- 4a, 5, 6, 7, 8, 8a-hexahydro quinazoline-2-thiol (Sathya et al 2009), 3,4-dihydropyrimidin-2(1H)-ones (Kumar et al 2010), 2-amino-5-mercapto-1,3,4-thiadiazole,2-mercaptothiazoline (Doner et al 2011) [90], 4- [5-(4-chlorophenyl) diazenyl]-2- hydroxybenzylideneamino)- 1,5-di methyl-2-phenyl-1H pyrazole-3-(2H)-one (Muthukrishnan et al 2014) have been investigated as corrosion inhibitor in acidic environments. Besides these, they are also important and useful intermediates in the synthesis of variety of heterocyclic compounds. The corrosion inhibition and adsorption behavior of 4-Amino Acetophenone Pyridine 2-Aldehyde (4AAPA) towards mild steel has been studied in acid medium (Karthik et al 2015).
Natural products can be considered as a good source for the corrosion inhibition purpose. Extracts of naturally occurring products contain mixture of compounds and are biodegradable in nature, these compounds having nitrogen and sulphur as constituent atoms are studied as corrosion inhibitor in HCl medium (Sivaraju & Kannan 2010). Some natural ingredients extracted from plants like henna leaf extract, green tea extract, mangrove wood tannins and flavonoid monomer have been introduced as new potential inhibitors (Lebrini et al 2011). However, such plants have their own limitations that may hinder them for inhibitor functioning. The phytochemical components of Musa Acuminata flower have been studied and known to be composed of tannins, flavonoids, saponins, alkaloids and phenols (Gunavathy & Murgavel 2013) which are responsible for inhibiting corrosion. Among them, corrosion inhibitors made of organic compounds have recently attracted to attention to obtain eco-friendly inhibitors (Umoru et al 2006).

Organic compounds with 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 these , Sapindus trifolianus, Acacia conjiana, Swertia aungustifolia and Quinoline based Cinchona alkaloids, Eucalyptus leaves and Eugenia jambolans 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 green 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 spectroscopy. Based on the literature survey, the nitrogen compounds were chosen as the inhibitors for the present research work were presented in Table 2.1.

**Table 2.1 Structure and physical properties of studied inhibitors**

<table>
<thead>
<tr>
<th>S. No</th>
<th>Name and Structure</th>
<th>Molecular Formula</th>
<th>Molecular Mass (g/mol)</th>
<th>Melting Point (°C)</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nicotinic acid N-oxide</td>
<td>C₆H₅NO₃</td>
<td>139.11</td>
<td>254</td>
<td>Water</td>
</tr>
<tr>
<td>2</td>
<td>Isonicotinic acid N-oxide</td>
<td>C₆H₅NO₃</td>
<td>139.11</td>
<td>296</td>
<td>Water</td>
</tr>
<tr>
<td>3</td>
<td>2-Picoline N-oxide</td>
<td>C₆H₅NO</td>
<td>109.13</td>
<td>65</td>
<td>Water</td>
</tr>
<tr>
<td>4</td>
<td>Pyridine N-oxide</td>
<td>C₅H₅NO</td>
<td>95.10</td>
<td>65</td>
<td>Water</td>
</tr>
<tr>
<td>5</td>
<td>4-Picoline N-oxide</td>
<td>C₆H₇NO</td>
<td>109.13</td>
<td>183</td>
<td>Water</td>
</tr>
<tr>
<td>6</td>
<td>2-Methyl 8-quinolinol</td>
<td>C₁₀H₉NO</td>
<td>159.19</td>
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<td>Water</td>
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Table 2.1 (Continued)

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<thead>
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<th>S. No</th>
<th>Name and Structure</th>
<th>Molecular Formula</th>
<th>Molecular Mass (g/mol)</th>
<th>Melting Point (°C)</th>
<th>Solubility</th>
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<tbody>
<tr>
<td>7</td>
<td>Methylmorpholine N-oxide</td>
<td>C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>117.15</td>
<td>182</td>
<td>Water</td>
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<td>8</td>
<td>Benzoin α-oxime</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>227.26</td>
<td>153</td>
<td>Ethanol &amp; Ether</td>
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<tr>
<td>9</td>
<td>2,6-Pyridine dimethanol</td>
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<td>139.15</td>
<td>113</td>
<td>Water</td>
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<td>2-Hydroxy-4-methyl quinoline</td>
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<td>159.18</td>
<td>222</td>
<td>Water</td>
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<tr>
<td>11</td>
<td>Benzimidazole</td>
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<td>171</td>
<td>Water &amp; Ethanol</td>
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<td>DMSO &amp; Ethanol</td>
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<td>2-Amino3-Hydroxy Pyridine</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O</td>
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<td>DMSO</td>
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<td>2-Pyrazine carboxylic acid</td>
<td>C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
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### Table 2.1 (Continued)

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<th>S. No</th>
<th>Name and Structure</th>
<th>Molecular Formula</th>
<th>Molecular Mass (g/mol)</th>
<th>Melting Point (°C)</th>
<th>Solubility</th>
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<td>C₆H₅ClN.HCl</td>
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### 2.4 OBJECTIVES OF THE PRESENT INVESTIGATION

The aim of the present study is to examine the following aspects.

1. To synthesize the nitrogen containing organic compounds.

2. To analyze the synthesized compounds by Infra-red Spectroscopy (IR), Proton-Nuclear Magnetic Resonance Spectroscopy (¹H NMR) and ¹³C - Nuclear Magnetic Resonance Spectroscopy (¹³C NMR) for their structural confirmation.
3. To study the corrosion inhibition behavior of the synthesized nitrogen containing organic compounds for mild steel in acidic solution (2N H₂SO₄).

4. To assess the performance of these inhibitors by weight loss measurement.

5. To study the performance of such inhibitors from polarization and impedance measurements.

6. To derive suitable adsorption isotherms for the selected inhibitors.

7. To explain the morphological characteristics of the mild steel surface in the corroding medium or 2N H₂SO₄ with and without these inhibitors at their optimal concentration levels.