CHAPTER 2

LITERATURE REVIEW.

Literature Review

2.1 Corrosion Inhibitors.

Due to its simplicity of application and lack of additional equipment requirements, the use of inhibitors is the most popular corrosion control technique.The inhibition effectiveness describes how much the presence of inhibitors slows the rate of corrosion,

$$\%IE = \frac{C^0_R - C^i_R}{C^0_R} x100 \qquad (2.1)$$

Here, C^0_R and C^i_R denote the corrosion rates in the absence and presence of the inhibitor, respectively.

2.1.1 Definition of Inhibition.

In the field of corrosion, inhibition has garnered a lot of attention. Inhibition is a method of protecting metallic materials from corrosive attack. When chemical compounds are given in small amounts to a hostile environment, they can reduce corrosion of the exposed metal.

2.1.2 Definition of Inhibitor.

An inhibitor is a chemical that, when added to acid solutions, limits metal loss, minimises the level of hydrogen embrittlement, protects the metal from pitting, eliminates over pickling and acid fumes created by excessive interaction between the acid and base metals, and reduces acid consumption. Corrosion inhibitors are substances that, when added in small amounts to a corrosive environment, slow the rate of corrosion. They prevent corrosion by acting as a barrier by forming an adsorbed layer or by slowing the cathodic and/or anodic processes. [(Vedula S. Sastri 1998)].

The National Association of Corrosion Engineers defines an inhibitor as a material that, even at low concentrations, retards corrosion [NACE (1965)]. Corrosion inhibitors are in charge of any corrosion retardation process or decrease in metal oxidation rate caused by the addition of a chemical substance to the system. [(Raja and Sethuraman 2008)].

Inhibitors are frequently simple to use and provide the benefit of in-situ application [P.B. Raja *et al*. (2008)] without creating a major disturbance to the process.

Corrosion inhibitors can be classified based on their (a) field of application (b) effect on the partial electrochemical reactions, and (c) reaction mechanism. Inhibitors function by one or more ways mentioned herein under.s.

1. adsorption as a layer on the corroding medium's surface.
2. The inhibitor generates a film by oxidising the base metal.
3. The inhibitor reacts with a potentially corrosive component in the environment.

The product is complex in aqueous media.

2.1.3 Classification based on the effect on partial electrochemical reactions.

Inhibitors of corrosion also work by slowing down partial electrochemical processes. This sort of inhibitor is categorized based on which partial reaction is most adversely affected. Based on this, there are three different categories of inhibitors:

- Anodic inhibitors

- Cathodic inhibitors

- Mixed inhibitors

2.1.3.1 Anodic inhibitors.

Anodic inhibitors are typically utilized in close to neutral solutions where corrosion products including oxides, hydroxides, or salts are created sparingly soluble corrosion products. They create passivating films that prevent the anodic metal dissolution reaction from occurring, or they assist in their creation. Passivating inhibitors are another name for anodic inhibitors. Corrosion may accelerate rather than be controlled when the concentration of an anodic inhibitor is insufficient. The kind and concentration of the aggressive ions determine the critical concentration above which inhibitors are effective [(Brooks *et al*. 1972)].

2.1.3.2 Cathodic inhibitors.

Cathodic inhibitors produce a decrease in corrosion potential. In this case, the cations migrate to the cathode surfaces, where they are chemically or electrochemically precipitated and block the surfaces.Cathodicprecipitators precipitate insoluble chemicals on the metal surface while increasing cathodic alkalinity. Cathodic precipitators that are most commonly used are calcium and magnesium carbonates. [(Saji 2010)].

2.1.3.3 Mixed inhibitors.

About 80% of inhibitors are organic substances known as mixed inhibitors that cannot be categorically classified as anodic or cathodic. The degree to which organic inhibitors adsorb to and coat the metal surface determines how effective they are. Adsorption is influenced by the inhibitor's structural makeup, the metal's surface charge, and the type of electrolyte. Physical adsorption, chemisorption, and film formation are the three potential mechanisms through which mixed inhibitors can shield the metal. The inhibitor's electrostatic affinity on the metal surface leads to physical (or electrostatic) adsorption. The adsorption of negatively charged (anionic)inhibitors is promoted when the metal surface is positively charged. A positively charged metal can be inhibited by positively charged molecules working with a negatively charged intermediary. Through this synergistic effect, quaternary ammonium cations limit the corrosion of iron in sulphuric acid that contains chloride ions. Inhibitors that are physically adsorb to surfaces interact quickly, but they can also be easily washed off. Generally, an increase in temperature makes it easier for physically adsorbed inhibitor compounds to desorb. The best inhibitors are those that chemically adsorb (chemisorb), which entails the transfer or sharing of charges between the molecules of the inhibitor and the metal surface.

Physical adsorption happens faster than chemisorption. Adsorption and inhibition both increase with temperature. The process of chemisorption is particular and not entirely reversible [(Vedula S. Sastri 1998)]. Adsorbed inhibitor molecules may experience surface reactions that result in the formation of polymeric films. Corrosion protection increases dramatically when the coatings progress from nearly two-dimensional adsorbed layers to three-dimensional films several hundred angstroms thick. Effective inhibitors are only adherent, insoluble coatings that prevent solution access to the metal. Conductive or non-conducting protective coatings are available.

Depending on the environment, inhibitors are also classified in to acid, base and neutral inhibitors.

This may be classified further in to;

Inorganic inhibitors and Organic inhibitors.

2.1.3.3.1 Inorganic inhibitors.

Addition of metal salts to the corrosive media is one approach for improving inhibition. The decrease in electropositive ions and subsequent deposition on the metal surface in this instance has the protective effect of lowering the overvoltage of the primary cathodic depolarization reaction. For mild steel in various acid solutions, the effect of inorganic anions with organic compounds has been investigated, and these are discovered to be efficient inhibitors.

Oxygen reduction at the cathodic sites is prevented in neutral solutions by the interaction of inhibitors with oxide-covered metal surfaces. These inhibitors defend the surface layers against aggression. Inhibitor displacement of pre-adsorbed water molecules is the first stage, which is followed by chemical or electrochemical surface reactions. Therefore, cathodic inhibitors are those that prevent the cathodic "reduction of oxygen to the surface of the metal." Anodic inhibitors, such as phosphates, silicates, borates, etc., stop anodic dissolution by forming passivating on the metal surface, like chromates and nitrites. When benzoate anions were present, a high surface coverage was seen, which favoured the development of a passive state [D.S. Azambuja and colleagues (1999)].

2.1.3.3.2 Organic inhibitors.

It has been observed that multiple-bond organic molecules with oxygen, nitrogen, and sulphur are effective corrosion inhibitors [(Moretti, Guidi, and Fabris 2013; Torres *et al.* 2014)] Based on their reactivity at the metal surface and potential shift, organic inhibitors can be classified as anodic, cathodic, or mixed types. Depending on the size, length of the carbon chain, aromaticity, conjugation, and kind of bonding atoms [(Günter Schmitt and Bedbur 1985)].

In alkaline solutions, metals that produce amphoteric oxide are susceptible to corrosion. Many organic substances are employed as metal inhibitors in fundamental solutions including tannin, gelatins, agar-agar, etc. Due to the development of metal complexes, substances like thiourea, substituted phenols, naphthol-diketone, etc., have been used as efficient inhibitors in basic solutions.

2.1.4 Classification based on reaction mechanism.

It is further classified into three types and is discussed below,

- Adsorption
- Passivation and

- Film formation

2.1.4.1 Inhibition by adsorption.

This particular class of inhibitors lowers metal corrosion by adhering to the surface and blocking the active sites. Adsorbed water coats surfaces of metal and oxide in contact with aqueous solutions. Inhibitors must replace one or more water molecules that have been adsorbed onto the metal surface for them to adhere there. As a result, the following diagram can be used to show an inhibitor's adsorption reaction:

$$\mathrm{Inh_{aq}} + x\,\mathrm{H_2O_{ads}} \longrightarrow \mathrm{H_2O_{aq}} + \mathrm{Inh_{ads}} \qquad (2.2)$$

where Inh stands for the inhibitor molecule, and aq and ads, respectively, stand for species in the aqueous phase and species adsorbed on the surface.

The stoichiometric coefficient x depends on the size of the inhibitor molecule and the structure of the metal surface.

2.1.4.2 Inhibition by passivation.

By inducing a significant anodic change in corrosion potential and bringing the metallic surface into the passivation condition, passivating inhibitors limit corrosion.

There are two types of passivating inhibitors;

i. Oxidizing anions, such as chromate, nitrite and nitrate, which can passivate iron in the absence of oxygen.

ii. Non-oxidizing ions such as phosphate, tungstate and molybdate that require oxygen to passivate iron.

By inducing a significant anodic change in corrosion potential and bringing the metallic surface into the passivation condition, passivating inhibitors limit corrosion.

2.1.4.3 Inhibition by film formation.

Through the creation of a barrier film made of a substance other than the inhibitor species, film forming inhibitors stop corrosion. These inhibitors only work with cathodic or anodic current, never both.They are further classified as

(i) Anodic film forming inhibitors and

(ii) Cathodic film forming inhibitors

By creating anodic coatings on the surface of metals, zinc and calcium salts prevent corrosion. In the presence of oxygen, a number of anodic film-forming inhibitors, such as benzoates, prevent corrosion. By reacting with the metal and other elements in the electrolyte solution, compounds of the phosphonate type produce cathodic coatings on the metal's surface.

2.1.5 Interface inhibitors (Vapour phase).

A chemical with a high vapour pressure that can stop the atmospheric corrosion of metallic materials is known as a vapour phase inhibitor. (for instance, benzotriazole, phenylthiourea, dicyclohexylammonium nitrate, etc.). They quickly evaporate and create a shield-like covering on the metal surface. In a certain environment of a specific range of acidity and pressure, they are able to form a stable connection with the metal surface and produce an impenetrable coating for corroding ions.

2.2.1 Quantum chemical calculations in corrosion inhibition studies.

Quantum chemical calculations have proven to be a very effective method for researching alloy and/or metal corrosion inhibition. A correlation between an organic corrosion inhibitor's efficiency and its electrical and spatial molecular structure has been observed[(Nnabuk Okon Eddy and Ebenso 2010)E. Ebenso *et al.(*2010)]. The functional groups, steric effect, orbital characteristics of the electrons donating, and electronic density of the donor atoms are all factors that affect an inhibitor's ability to inhibit [(Quraishi and Sardar 2002; Stupnišek-Lisac, Podbršček, and Sorić 1994)].The DFT (Density Functional Theory) states that the HOMO and LUMO frontier MOs have a relationship with the inhibitor's capacity to react [(Nnabuk Okon Eddy and Ebenso 2010)]. Greater electron ability is caused by the adsorbent's higher HOMO energy (E_{HOMO}) [(Lee, Yang, and Parr 1988)]. Low LUMO energy (E_{LUMO}) denotes a simple electron acceptance by the acceptor.

Optimization was used to calculate the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), and the energy gap (E_{LUMO} - E_{HOMO}) between LUMO and HOMO. The inhibitor molecules' adsorption centres, which are what cause them to interact with surface metal atoms, can be predicted using FOT (Frontier Orbital Theory) [(Awad, Mustafa, and Elnga 2010)]. Due to the inverse dependency of stabilisation energy on the difference in orbital energy, the term including the frontier MO may contribute more than anything else. It was also crucial to take into account the difference between the molecules' HOMO and LUMO energy levels. According to reports, the best corrosion inhibitors are typically organic compounds that absorb free electrons from the metal as well as supply electrons to the metal's empty orbital [(Obi-Egbedi, Obot, and El-Khaiary 2011)].

According to Gece and Bilgic [(Gece and Bilgiç 2010)], the corrosion inhibition efficacy altered as the location of N atoms changed. The polarity is revealed by the dipole moment. When the molecule's polarity is at its highest and the dipole moment is at its greatest. According to research on corrosion inhibition, when the inhibitor's dipole moment increases, the percentage of inhibition efficiency rises [(Nnabuk O Eddy *et al.* 2011)]. Some scientists have previously claimed that greater inhibition efficiency is caused by smaller values of E and greater values of the dipolemoment [(V. S. Sastri and Perumareddi 1997)]. Since it will take less energy to remove an electron from the final occupied orbital, energy gaps with lower values will produce better inhibition efficiency.

2.3 Hetero-Cyclic Compounds as Corrosion Inhibitors.

Organic substances that have a donor site for adsorption on a metal surface are effective corrosion inhibitors. The best inhibitors of corrosion are heterocyclic compounds with N and S atoms. According to [(Talati and Gandhi 1983; Elmorsi and Hassanein 1999; Popova and Christov 2006)], and [(Raicheva, Aleksiev, and Sokolova 1993)Raicheva *et al.* (1993)], heterocyclic compounds, particularly those containing nitrogen, offer a promising class of corrosion inhibitors.The inhibitive properties of heterocyclic compounds with both nitrogen and sulphur atoms are superior than those of compounds with only one of the two atoms [(Ajmal, Mideen, and Quraishi 1994)];[(Abd-El-Nabey *et al.* 1996; Quraishi and Sardar 2003; 2002)]. These compounds' corrosion-inhibiting ability is a result of their molecular makeup.Adsorption of these molecules on the metal surface is greatly assisted by their planar structure and the presence of lone pair electrons on heteroatoms. The formation of an effective thin layer barrier across the metal surface as a result of compound adsorption prevents metal disintegration in acidic solutions.

An overview of inhibitors.

Researchers have a significant difficulty as a result of the widespread issue of scale formation in machinery and equipment in industries. Cleaning the equipment with mineral acids is crucial to preventing the growth of scales. But because these acids are so aggressive, inhibitors are frequently utilized to make them less aggressive.Schmitt [(G. Schmitt 1984)] went into great detail regarding the several types of inhibitors that are advised to prevent metallic materials, particularly ferrous metals and alloys, from corroding in acid solutions while pickling, acid cleaning, removing scale, and acidizing oil and gas wells.

A review of the literature reveals that phosphorous, sulphur, nitrogen, and oxygen are commonly found in the structures of many organic corrosion inhibitors that are efficient in preventing corrosion in a variety of metals and alloys subjected to acid solutions. HananeHamani*et al*. investigated Thecorrosion prevention of azomethine against mild steel [(Zheng *et al*. 2014)].Xingwen Zheng et al. studied Thecorrosion inhibition performance of 1-butyl-3-methyl-1H-benzimidazolium iodide for mild steel in H_2SO_4 [(Zheng *et al*. 2014)]. Matjaz Finsgar *et al*. studied 2-mercaptobenzoxazole as a copper corrosion inhibitor in HCl [(Zheng *et al*. 2014)]. Nam *et al*. studied the behaviour of praseodymium 4-

hydroxycinnamate against oxygen corrosion of steel in NaCl [(Nam *et al.* 2014)].[V.V. Torres and V.A. Rayol] studied the synthesized thioureas as corrosion inhibitor for mild steel in HCl [(Torres *et al.* 2014)]. Pyridyl substituted triazoles as new and effective corrosion inhibitors for mild steel in HCl was studied by K.R. Ansari [(Ansari, Quraishi, and Singh 2014)]. Bin Xu *et al.,*described the experimental and theoretical evaluation of two pyridine carboxaldehyde thiosemicarbazone compounds as corrosion inhibitors.[(Xu *et al.* 2014)]. D. Daoud studied the newly synthesized thiophene Schiff base as corrosion inhibitor on mild steel [D. Daoud *et al.*(2009)]. Electrochemical impedance evaluation of pantoprazole as corrosion inhibitor was reported by Espinoza-Vazquez *et al.,* [(Espinoza-Vázquez *et al.* 2014)]. Thermodynamic and electrochemical investigation of pantoprazole was reported by M.A. Quraishi *et al.,* [(Sudheer and Quraishi 2013)]. Karthik and Sundaravadivelu had evaluated the corrosion inhibition of esomeprazole in H_2SO_4 [(Karthik and Sundaravadivelu 2013)]. Experimental and theoretical examination of lansoprazole as corrosion inhibitor was undertaken by Karthick *et al.* [(Karthik and Sundaravadivelu 2013)]. Inhibiting effects of rabeprazole sulfide on the corrosion of mild steel in HCl medium was reported by Pavithra *et al.* [(Pavithra, Venkatesha, and Punith Kumar 2013)]. H. Tian *et al.* has studied the novel non-toxic thiadiazole derivatives as corrosion inhibitors [(Tian *et al.* 2013)]. Pan *et al.,* examined the inhibitive properties of 2-amino-5-(4-pyridinyl)-1,3,4-thiadiazole monolayers on copper surface [(Pan *et al.* 2013)]. Hong and Chen investigated the inhibitory effect of trithiocyanuric acid against copper [(Hong *et al.* 2013)]. M. Finsgar had reported the EQCM and XPS analysis of 1,2,4-triazole and 3-amino-1,2,4-triazole as copper corrosion inhibitors

[(Finšgar 2013)]. El Adnani *et al.* had carried out the theoretical study of 7-R-3methylquinoxalin-2(1H)-thiones as corrosion inhibitor in HCl [El Adnani *et al.* (2013)]. Doner *et al.,* investigated the corrosion inhibition of 3-[(2-hydroxy-benzylidene)-amino]-2-thioxo-thiazolidin-4-one against mild steel in acid medium [(Tourabi *et al*. 2013)]. C.M. Goulartb *et al.* evaluated the corrosion inhibition of semicarbazones and thiosemicarbazones. Tourabi *et al.,* examined the inhibition potential of 3,5-bis(2-thienylmethyl)-4-amino-1,2.4-triazole by electrochemical and XPS studies [(Tourabi *et al.* 2013)]. Experimental and theoretical studies of two new benzothiazine derivatives were reported by Ghailane *et al.,* [(Ghailane *et al*. 2013)]. Sudheer and Quraishi investigated the electrochemical and theoretical effects of triazole derivatives on copper corrosion inhibition in HCl media. [(Sudheer and Quraishi 2013)]. Hegazy *et al.*reported the corrosion inhibition of carbon steel using novel dodecane compounds as acid pickling agents. Kovacevic and Kokalj studied the relation between adsorption bonding and corrosion inhibition of azole molecules on copper [(Kokalj 2013)]. Markhali *et al.* used electrochemical impedance spectroscopy and electrochemical noise measurements to investigate the corrosion inhibition of azole compounds on stainless steel. Qian et al. evaluated the synergistic effect of polyaspartic acid and iodide ions on mild steel corrosion inhibition in H_2SO_4. [(Qian *et al*. 2013)]. Yan and Wang investigated the molecular dynamics simulation of corrosive species transport in imidazoline inhibitor films with varying alkyl chain lengths [(Tao *et al*. 2009)]. Tao *et al.* investigated the corrosion prevention of mild steel by oxo-triazole derivatives in acidic solution. [(Tao *et al*. 2009)]. Kokalj reported the formation and structure of inhibitive molecular film of imidazole on iron surface [(Kokalj 2013)]. Jevremovic had evolved a novel method to mitigate the top-line corrosion in wet gas pipelines by corrosion inhibitor within a foam matrix [(Jevremović *et al*. 2013)]. Behpour and Mohammadi examined the inhibitory properties of aromatic thiol self-assembled monolayers for corrosion protection. [(Behpour and Mohammadi 2012)]. Levin *et al.* reported some bioorganic compounds as copper corrosion inhibitors in hydrocarbon media [Levin *et al.* (2012)].Hong et al. investigated the inhibitory impact of 4-amino antipyrine on copper corrosion in a 3 wt.% NaCl solution [(Hong *et al*. 2012)]. Izquierdo *et al.* examined the anti-corrosion performance of 2-mercaptobenzimidazole on copper through electrochemical measurements [(Izquierdo *et al.* 2012)]. Niamien reported the corrosion inhibition effect of some benzimidazole derivatives for [Niamien*et al*. (2012)]. Li *et al.* reported allyl thiourea as a corrosion inhibitor for cold rolled steel in H_3PO_4 solution [(Li *et al.* 2012)]. Caliskan and Akbas investigated the corrosion prevention of austenitic stainless steel in hydrochloric acid by certain pyrimidine compounds. [Caliskan and Akbas *et al*. (2012)]. Zhang *et al.* studied the performance of corrosion inhibition of 2-(4-pyridyl)-benzimidazole for mild steel in hydrochloric acid [(F. Zhang et al. 2012)]. To *et al.* studied the layered double hydroxides as containers of inhibitors in organic coatings for corrosion protection of carbon steel [(Musa, Jalgham, and Mohamad 2012)]. Musa *et al.* investigated the molecular dynamic and quantum chemistry calculations for phthalazine derivatives as mild steel corrosion inhibitors in 1 M HCl. [(Musa, Jalgham, and Mohamad 2012)]. Heydari and Javidi studied the corrosion inhibition and adsorption behavior of an amidoimidazoline derivative on API 5L X52 steel in CO_2 saturated solution

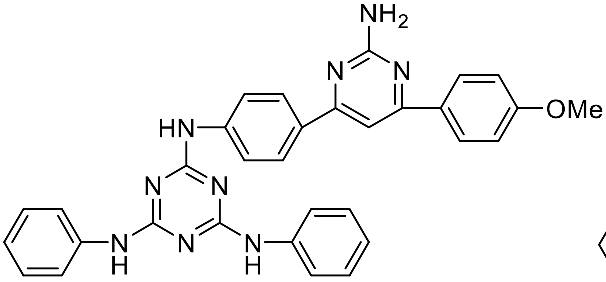
[(Heydari and Javidi 2012)]. Fragoza-Mar *et al.* studied the corrosion inhibition activity of 1,3-diketone malonates for mild steel in HCl (Jevremović *et al*. 2013)]. Jevremovic reported that the mixture of dicyclohexamine and oleylamine as corrosion inhibitor for mild steel in NaCl solution [Jevremovic *et al*.(2012)]. A.K. Singh studied the inhibition of MS corrosion in HCl by 3-(4-((Z)-indolin-3-ylideneamino) phenylimino) indolin-2-one (Finšgar 2013) . A review of promising novel corrosion inhibitors in acid media was reported by Gece. Khiati*et al.* studied corrosion inhibition of copper in neutral chloride media by 1,2,4-triazole [Khiati *et al*. (2011) 102]. Finsgar and Milosev reported the corrosion study of copper in the presence of benzotriazole and its hydroxy derivative [(Finšgar 2013)]. Karthik*et al.*studied the inhibition of mild steel corrosion by 1,3-bis-(morpholin-4-yl-phenyl-methyl)-thiourea in hydrochloric acid medium [(Karthik and Sundaravadivelu 2013)]. Khodyrev studied the inhibition action of ammonium salts of dialkyldithiophosphoric acid on carbon dioxide corrosion against mild steel [(Khodyrev *et al.* 2011)]. Feng *et al.* reported the corrosion inhibition of carbon steel by imidazoline derivative [Feng *et al*. (2011)]. Various researchers [Negm *et al*. (2012), Hegazy *et al.* (2012), K.R. Ansari *et al*. (2012), D.K. Yadav *et al*. (2012), J.J. Fu *et al*. (2012), N.A. Negm *et al*. (2011)] used nitrogen containing onium salts as corrosion inhibitors in acid media.

2.3.1 Triazine-based inhibitors.

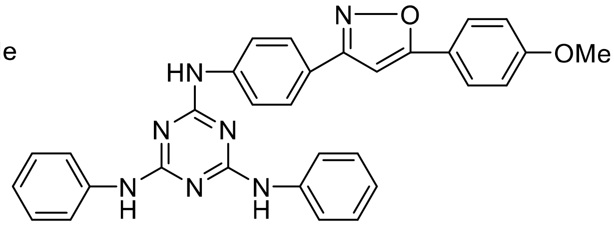
Triazines attract a great deal of attention due to their remarkable reactivity and thewide range of functionalized azaheterocyclic structures that can be prepared using them as starting materials. Triazines and their synthetic derivatives are interesting for various applications as bioactive compounds, complexation agents, useful tags for binding to different substrates, and intermediates in the construction of functional materials. However, several reports describe their potential as cardiotonic [(Kreutzberger and Kochanowski 1988)], neuroleptic [(Kreutzberger and Kochanowski 1988)]. [(Kreutzberger and Kochanowski 1988)], antihistaminergic [(Mohr, Buschauer, and Schunack 1986)], anti-HIV [(Brzozowski and Sączewski 2002)], antiviral [(Angelucci *et al.* 1963)] and anticancer [(Ono *et al.* 1996)] agents.

Triazines anditsderivativehavebeeninvestigatedaseffectivecorrosioninhibitorsforferrous alloys. M. Yadav *et al.* have been investigated the inhibition effect of two synthesized triazine derivatives, namely: (APTT) and (MITT) on N80 steel in a 15% HCl solution using gravimetric measurement, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques [(M. Yadav *et al*. 2015)]. The efficiency of inhibition was discovered to rise with increasing inhibitor concentrations and decrease with rising temperature. The inhibitors' inhibitory abilities follow the order: APTT > MITT. The results showed that triazine derivative APTT (IE 87.7%) is more effective than MITT (IE 86%) at

150 ppm. All these in ihibitors are mixed type, and the adsorption obeyed the Langmuir adsorption isotherm.

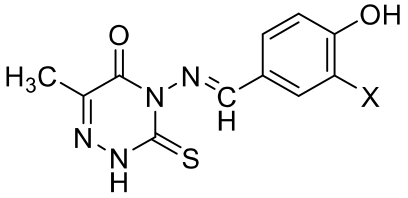


(APPTT)



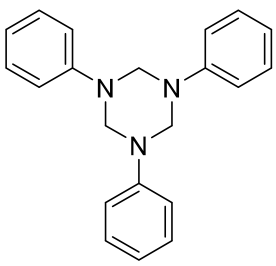
(MITT)

M. Prajila *et al* .STUDIED The inhibitory behaviour of three distinct triazine-based Schiff's bases, HMMT, DHMMT, and MHMMT, for mild steel corrosion in sulphuric acid has been studied utilising weight loss, electrochemical tests, SEM, spectroscopic studies, and basic computational research. [(Prajila, Ammal, and Joseph 2018)]. In the case of these three inhibitors, the inhibition efficacy rose with increasing inhibitor concentration but declined with increasing temperature and acid concentration. The order of inhibitory efficiency predicted by band energy values agrees well with the results of weight loss and electrochemical tests. Polarization tests revealed that these inhibitors have a heterogeneous sort of behaviour.

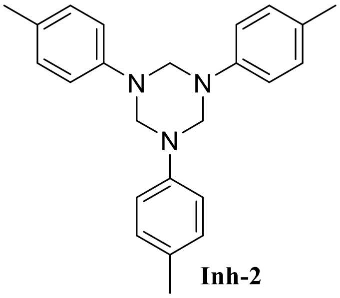


HMMT (X = H), DHMMT (X = OH) and MHMMT (X = OMe)

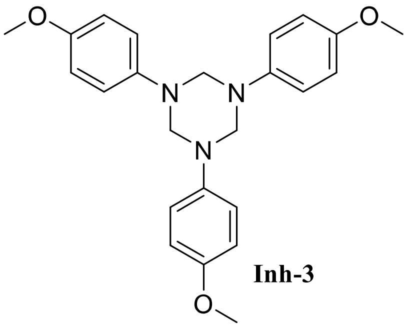
S. K. Shukla *et al.* have studied the inhibition effect of Five triazines based inhibitor namely: Hexahydro-1,3,5-triphenyl-s-triazine (Inh-1), Hexahydro-1,3,5-p-tolyl-s-triazine (Inh-2), Hexahydro-1,3,5-p-methoxyphenyl-s-triazine (Inh-3), Hexahydro-1,3,5-p-aminophenyl-s-triazine (Inh-4) and Hexahydro-1,3,5-p-nitrophenyl-s-triazine (Inh-5)mild steel in 1M HCl solution using weight loss, polarization resistance, Tafel polarization and electrochemical Impedance spectroscopy techniques[(Shukla, Singh, and Quraishi 2012)]. All the triazines showed the highest inhibition efficiency at 300 ppm concentration. The inhibition efficiency of the synthesized inhibitors followed the order Inh4 > Inh3 > Inh2 > Inh1 > Inh5. The presence of NH_2 group significantly increased the inhibition efficiency of Inh4 while withdrawing group NO_2 reduced the inhibition efficiency of Inh5. Potentiodynamic polarizations suggest that triazines are mixed type in nature.



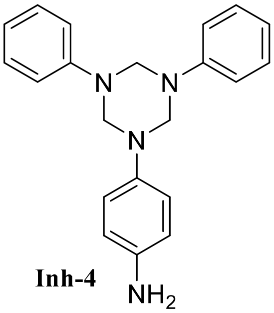
Inh-1



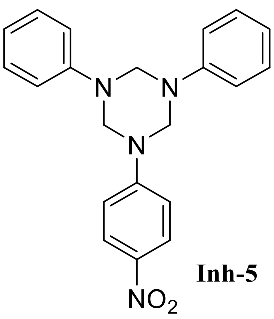
Inh-2



Inh-3

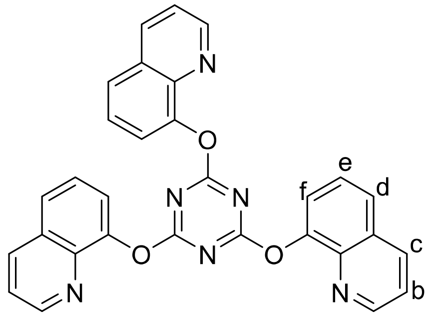


Inh-4

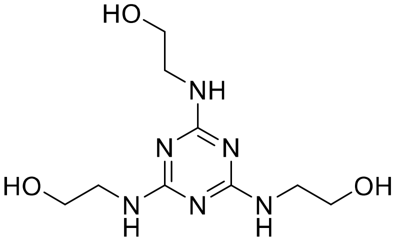


Inh-5

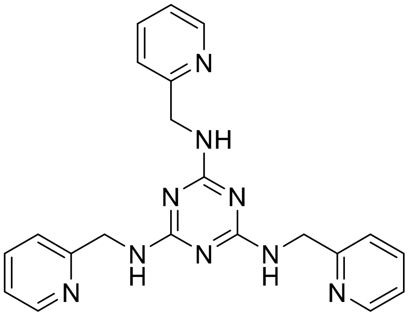
Recently, Ayman El-Faham *et al.* have evaluated the effect of the triazinemoiety structure of the side chain on corrosion inhibition of three sym-Trisubstituted 1,3,5-Triazine Derivatives on steel in 1mol L^{-1} HCl **[**(El-Faham *et al.* 2016)]. The electrochemical results showed that T3Q, T3AMPy, and T3EA are effective organic inhibitors and can be classified as mixed type inhibitors. The results showed that the more nitrogen atoms in the inhibitor's terminal groups, the better the corrosion protection performance; hence, T3Q and T3AMPy provided superior protection for steel than T3EA, which has an oxygen atom in its terminal side chain of the triazinemoiety.



T3Q; 4(86%)



T3EA; 6 (83%)

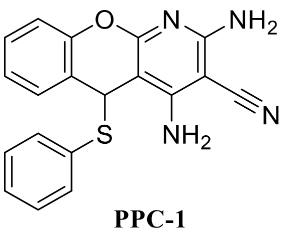


T3AMPy; 8 (85%)

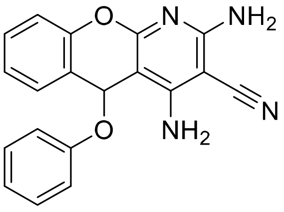
2.3.2 Naphthyridne based inhibitors.

The naphthyridine group of chemicals has piqued the curiosity of researchers due to a wide range of intriguing biological properties. Antibacterial, antimycobacterial, antiallergitic, anticancer, antiaggressive, antiinflammatory, antihypertensive, and antimalarial actions distinguish them as physiologically inspired compounds. [(Gohil and Patel 2016)].

K.R. Ansari *et al.* investigatedtheinhibitioneffectof chromeno pyridine derivatives namely: 2,4-diamino-5-(phenylthio)-5H-chromeno[2,3-b] pyridine-3-carbonitrile (PPC-1) and 2,4-diamino-5-phenoxy-5H-chromeno[2,3-b] pyridine-3-carbonitrile (PPC-2) as potential environmentally friendly corrosion inhibitors for N80 steel in 15% hydrochloric acid (HCl) [(Ansari and Quraishi 2015)].Techniques such as gravimetric, electrochemical impedance spectroscopy (EIS), Tafel polarizations, scanning electron microscope (SEM), and atomic force microscopy (AFM) have all been used. PPC-1 and PPC-2 inhibition efficiencies are 92.4% and 82.1%, respectively, at 200 mgL^{-1}.



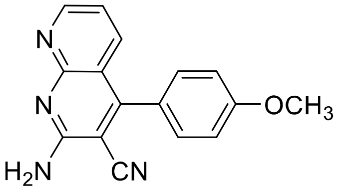
PPC-1



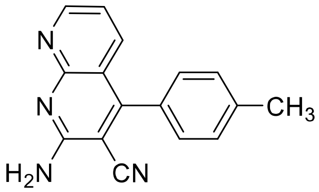
PPC-2

Many other researchers have also carriedout corrosion inhibition test of different chromeno naphthyridine derivatives oncarbon steel in acid solution. K.R. *et al.* have investigated that inhibition effect of three naphthyridine derivatives, namely 2-amino-4-(4-methoxyphenyl)-

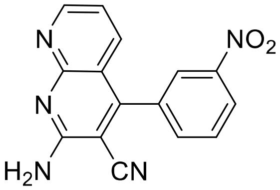
1,8- naphthyridine-3-carbonitrile (ANC-1),2-amino-4-(4-methylphenyl)-1,8-naphthyridine-3-carbonitrile (ANC-2), and 2-amino-4-(3-nitrophenyl)-1,8-naphthyridine-3-carbonitrile (ANC-3) as corrosion inhibitors for N80 steel in 15% HCl [(Ansari and Quraishi 2015)].HCl by using gravimetric, electrochemical techniques (EIS and potentio-Dynamic polarization), SEM, EDX, and quantum chemical calculation.The order of inhibition efficiency is ANC-1>ANC-2>ANC-3. Potentiodynamic polarization reveals that these inhibitors are mixed type with predominant cathodic control. Studied inhibitors obey the Langmuir adsorption isotherm.



ANC-1

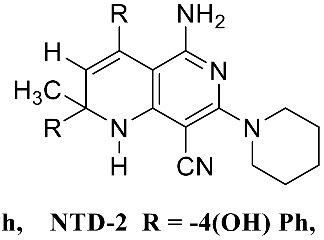


ANC-2



ANC-3

Verma *et al*. investigated the effect of three naphthyridines (NTDs) on the acidic dissolving of mild steel was studied using experimental methods. [(Verma *et al*. 2018)]. The protection abilities of NTD molecules improve with concentration. At a dose of 4.11 mol/L, the NTD-3 molecule had a maximum inhibitory efficiency of 98.69%. The inhibitory efficiency of NTDs compounds were as follows: NTD-1 (96.1%) < NTD-2 (97.4%) < NTD-3 (98.7%).

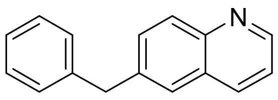


NTD-1 R = -Ph, NTD-2 R = -4(OH) Ph, NTD-3 R = 2,4(OH) Ph

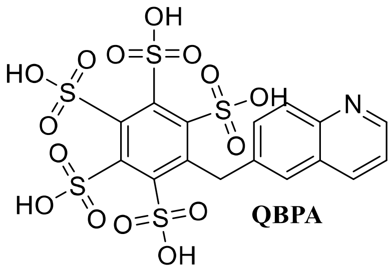
2.3.3 Quinolines based derivatives.

Quinoline [Abadi *et al.*], also known as 1-aza-napthalene or benzo[b]pyridine, is a heterocyclic aromatic chemical containing nitrogen. Quinoline nucleus is found in a variety of natural compounds (Cinchona Alkaloids) and pharmaceutically active drugs with diverse biological activities. Quinoline is antimalarial, antibacterial, antifungal, anthelmintic, cardiotonic, anticonvulsant, anti-inflammatory, and analgesic. Several chemicals that appear to be promising [(Achary *et al.* 2008)].

The inhibition performance of two quinoline derivatives, 6-benzylquinoline (BQ) and 6-(quinolin-6-ylmethyl) benzene-1,2,3,4,5-pentasulfonic acid (QBPA), on mild steel in 1M HCl was investigated using weight loss, electrochemical measurements, scanning electron microscopy (SEM), and atomic force microscopy (AFM). [(Jiang *et al.* 2018)**].** All trial results showed that BQ and QBPA significantly improved the corrosion resistance of mild steel, with QBPA outperforming BQ.



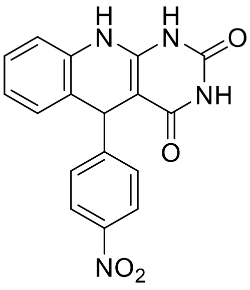
BQ



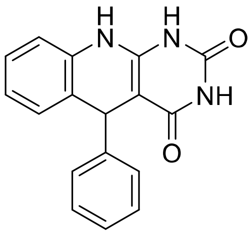
QBPA

ChandrabhanVerma *et al.* investigated The inhibition of mild steel corrosion in 1 M HCl by four 5-arylpyrimido-[4,5-b]quinoline-diones (APQDs),namely 5-(4-nitrophenyl)-5,10-

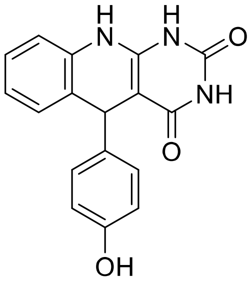
dihydropyrimido [4,5-b]quinoline-2,4(1H,3H)-dione (APQD-1), 5-phenyl-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione (APQD-2), 5-(4-hydroxyphenyl)-5,10-dihydropyrimido-[4,5-b]quinoline-2,4(1H,3H)-dione (APQD-3) and 5-(2,4-dihydroxyphenyl)-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione (APQD-4) using weight loss, electrochemical, surface, and quantum chemical calculations and molecular dynamics simulation methods [(C.Verma *et al.* 2016)]. Among the chemicals tested, APQD-4 had the best inhibitory efficacy of 98.30% at 20 ppm concentration. The investigated compounds significantly retarded the corrosion of mild steel in 1 M HCl by adsorbing onto the steel surface, and the adsorption data matched the Langmuir adsorption isotherm.



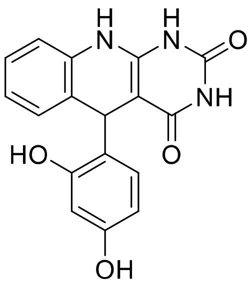
APQD-1



APQD-2

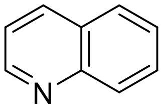


APQD-3

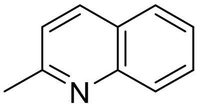


APQD-4

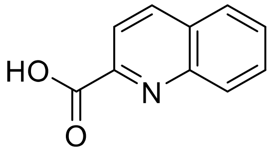
Eno E. Ebenso *et al.* tested Quinoline (QL) and its derivatives, namely quinaldine (QLD) and quinaldic acid (QLDA), as inhibitors for the corrosion of steel in 0.5 M HCl by weight loss method at 30 and 40°C [(Nnabuk Okon Eddy and Ebenso 2010)]. The results suggest that the order of inhibition efficiency is QLDA > QLD > QL. The adsorption of inhibitors on the steel surface follows the Langmuir and kinetic thermodynamic theories.



Quinoline



Quinaldine



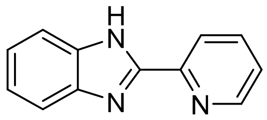
Quinaldic acid

2.3.4 Imidazole based inhibitors.

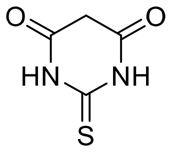
Imidazole, an aromatic compound comprised of three carbon and two nitrogen atoms, has a high solubility in aqueous conditions due to its strong polarity. The two N atoms and the aromatic ring provide two excellent anchoring sites for collaboration with metal surfaces. [Holze *et al*. (1993)]. The addition of a benzene ring or other functional groups to an imidazole molecule can boost its corrosion inhibition abilities. Benzimidazole is a well-known heteroaromatic bicyclic compound that has a benzene ring adjacent to an imidazole ring. Hoebrecker identified it and it is a component of Vitamin B12 [(Obot and Edouk 2017)]. In recent years, there has been a lot of interest in the synthesis of benzimidazoles. The benzimidazole moiety is found in a wide variety of natural substances and has significant medicinal significance. Uses include potential anticancer medicines [Denny *et al*.(1990)], antimicrobial agents [(Fonseca, Gigante, and Gilchrist 2001)], and angiotensin II inhibitors [(Kohara *et al*. 1996)].

Ikenna B. *et al*. A time-evolution study was carried out on 2-(2-pyridyl) benzimidazole (2PB) as a CO_2 corrosion inhibitor for API X60 steel in a synthetic brine solution.

Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) techniques were used in this study. [(Onyeachu, Obot, and Adesina 2020)]. The results reveal that 2.56 mM of 2PB might deliver up to 88.3% inhibitory efficiency in the synthetic brine solution after 12 hours at 4000 rpm. When using PDP, the addition of 0.14mM thiobarbituric acid (TBA) boosts 2PB performance to 95.6%.

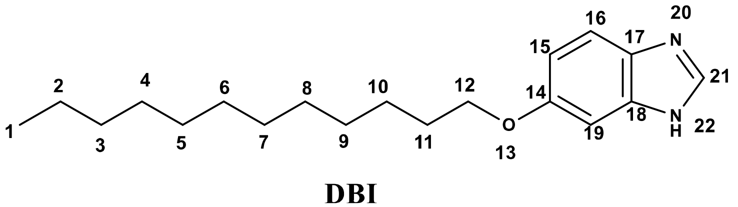


2-(2-Pyridyl)benzimidazole (2PB)



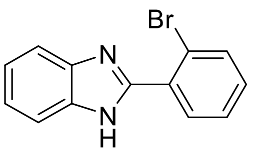
Thiobarbituric acid (TBA)

Dongqin Zhang *et al.* investigated the inhibitory performance of a novel benzimidazole derivative, 6-(dodecyloxy)-1H-benzo[d] imidazole (DBI), in 1 M HCl. The adsorption of DBI on metal surfaces was investigated using computational chemistry. [(D. Zhang *et al.* 2016)].The molecule form of DBI may interact more firmly with the iron surface than the protonated version. According to these findings, the long-chain alkyl-substituted benzimidazole derivative has a lot of potential for application as a corrosion inhibitor.

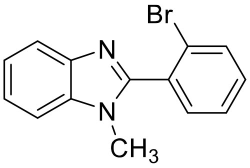


DBI

I.B. Obot *et al.* used an experimental and theoretical method to examine the surface adsorption features and corrosion inhibition behaviour of two novel benzimidazole derivatives, 2-(2-Bromophenyl)-1H-benzimidazole (BPBA) and 2-(2-Bromophenyl)-1-methyl-1H-benzimidazole (BPMA). [(Obot *et al*. 2015)]. All of the results showed that BPMA is a better mild steel corrosion inhibitor than BPBA in 0.5M HCl.

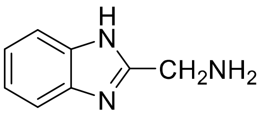


BPBA

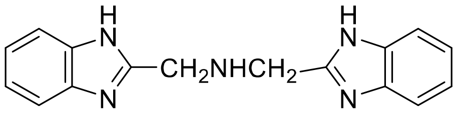


BPMA

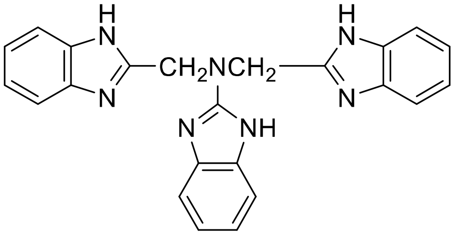
Yongming Tang *et al*. evaluated the inhibition performance of three new benzimidazole derivatives as mild steel inhibitors in 1.0 M HCl: 2-aminomethyl benzimidazole (ABI), bis (2-benzimidazolylmethyl) amine (BBIA), and tri (2-benzimidazolylmethyl) amine (TBIA). [(Tang *et al*. 2013)]. The efficacy of inhibition improves as the number of benzimidazole segments in the molecules increases (TBIA > BBIA > ABI). Inhibitor protection efficiency is affected by inhibitor concentration, temperature, and hydrochloric acid concentration.



ABI



BBIA



TBIA

2.4 The scope and importance of corrosion inhibitor technology.

Heterocyclic compounds are frequently utilized as corrosion inhibitors in a variety of sectors to prevent corrosion in acidic environments. The oil and gas exploration and production sector, petroleum refining business, chemical industry, heavy industrial manufacturing industry, water treatment industry, and additive product industry are the key industries that use corrosion inhibitors. Corrosion inhibitors are also utilized in numerous systems, such as cleaning pads, cooling systems, pipelines, chemical processes, steam generators, ballast tanks, and many consumer products. One of the most notable characteristics of the corrosion inhibitor is that it does not disrupt the process. Inhibitors are primarily used to protect a single metal or combination of metals in a closed or recirculating system.

2.5 Objective of present study.

The proposed research work will focus on the following points:

1. Synthesis of efficient organic corrosion inhibitors.

2.The corrosion inhibition of the synthesized inhibitors for N80 steel, and mild steel in 15% HCl, 3.5% NaCl saturated with CO_2, and 20% H_2SO_4 solutions was investigated using weight loss measurements, potentiodynamic polarization, electrochemical impedance spectroscopy techniques, and contact angle measurement, respectively.

3. Analysis of surface morphology of uninhibited and inhibited steels samples by using SEM, EDX SECM, and AFM techniques.

4. Quantum chemical calculations using Density functional theory (DFT) to correlate the experimental data.

5. Study of the mechanism of corrosion inhibition on the basis of the above studies.