

Heterocyclic Compounds as Corrosion Inhibitors for Mild Steel: A Review

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Abstract: Corrosion inhibition of mild steels is an importance topic since the use of mild steel is inevitable in chemical processing, petroleum production, refining, pipelines, mining etc. The low cost, high mechanical strength and availability are the main advantages of the use of mild steels. Corrosion of mild steels occurs when it exposes to aggressive environment. Numerous corrosion inhibitors are developed for the control of corrosion of metals and alloys. Compounds containing N, S and O are most studied due their higher inhibition ability. Particularly in recent years, heterocyclic compounds have attracted huge attention due its simple preparation and superior corrosion inhibition activity towards mild steel in acidic environments. Therefore, the aim of the present review is to highlight the recent work carried out using heterocyclic compounds and its derivatives for steel protection in different corrosive environments. In addition, heterocyclic compounds reported for the corrosion inhibition of steel in CO₂ saturated brine environment are also highlighted. Detail mechanisms involved in the inhibition processes are also discussed.

Keywords: Heterocyclic compounds; Mild steel; carbon Steel; Acidic environment; CO₂ corrosion; Adsorption

1. Introduction

Mild steels are most commonly used as construction material for down-hole tubing, flow lines and transmission pipelines in the petroleum industry. The mild steel materials can be easily corroded by their environments. The corrosion of steel causes huge investment for its inspection, repair and replacement of corroded materials. In petroleum industries, the product from the well is transported as a mixture of oil, salt water and natural gases.^[1-3] Under acidic environment, the mild steel would corrode faster and form oxides as products. Hydrochloric acid and sulphuric acid (HCl and H₂SO₄) are the widely used chemicals in the petroleum industries. Alike, in oil gas industries carbon dioxide (CO₂) creates corrosion, and the action was noticed in 1940 by Ikeda et al.^[4] CO₂ gas present in natural gases dissolves in brine solution and forms a weak carbonic acid which results in steel pipeline corrosion. In order to control steel corrosion, inhibitors are the one of the most practical and cost effective methods currently employed. The inhibitors may be organic molecules containing polar groups including N, S and/or O atoms and heterocyclic compounds with polar functional groups and conjugated double bonds.^[5-7] The inhibitor molecules can adsorbed on the metal surfaces and block the active sites on the surface and thereby reduce the corrosion rate.^[8-11] In addition, the N, S and/or O atoms can form chemical bond with the Fe and would protect the steel surface in aggressive environments.

Corrosion inhibitors have been considered to be the first line of defence against corrosion in oil gas industries.^[12-14] Recently, N-containing organic compounds are proposed as potential inhibitor for steel corrosion in saturated CO₂ environment. Particularly, imidazoline and its derivatives are getting more attention, due to its excellent adsorption character and chemical film formation properties.^[15] Villamizar et al.,^[16] studied the imidazolines inhibition efficiency on carbon steel corrosion in CO₂ environment. Nitrogen based organic compounds such as benzimidazole, imidazoline amides, imidazoline amino amides and their derivatives have been successfully used as inhibitor in oil and gas industries.^[17-21] The inhibition mechanism of benzimidazole derivatives for the corrosion of metals in acidic environments has been documented. Based on this concept, heterocyclic compounds, particularly, benzimidazole and its derivatives would acts as strong base due to its pyridine-like nitrogen, which can serve as electron donor to Fe-surface and product it form the further damage of metal. On the other hand, Fe³⁺, Fe²⁺ and metallic Fe would behaves as acid and acts as an electron acceptor. Metals with higher oxidation state shows more acidic nature, interaction between metal and heterocyclic compounds was due to long range electrostatic forces.^[22] Guo et al.,^[23] reported heterocyclic imidazoline derivatives as mixed type corrosion inhibitor and it affects both the anodic and cathodic reactions. They found that the increase in the inhibitor concentration increases the corrosion inhibition efficiency (IE) and the adsorption

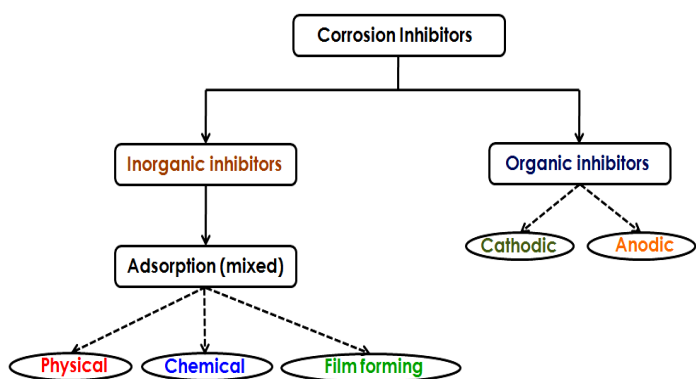
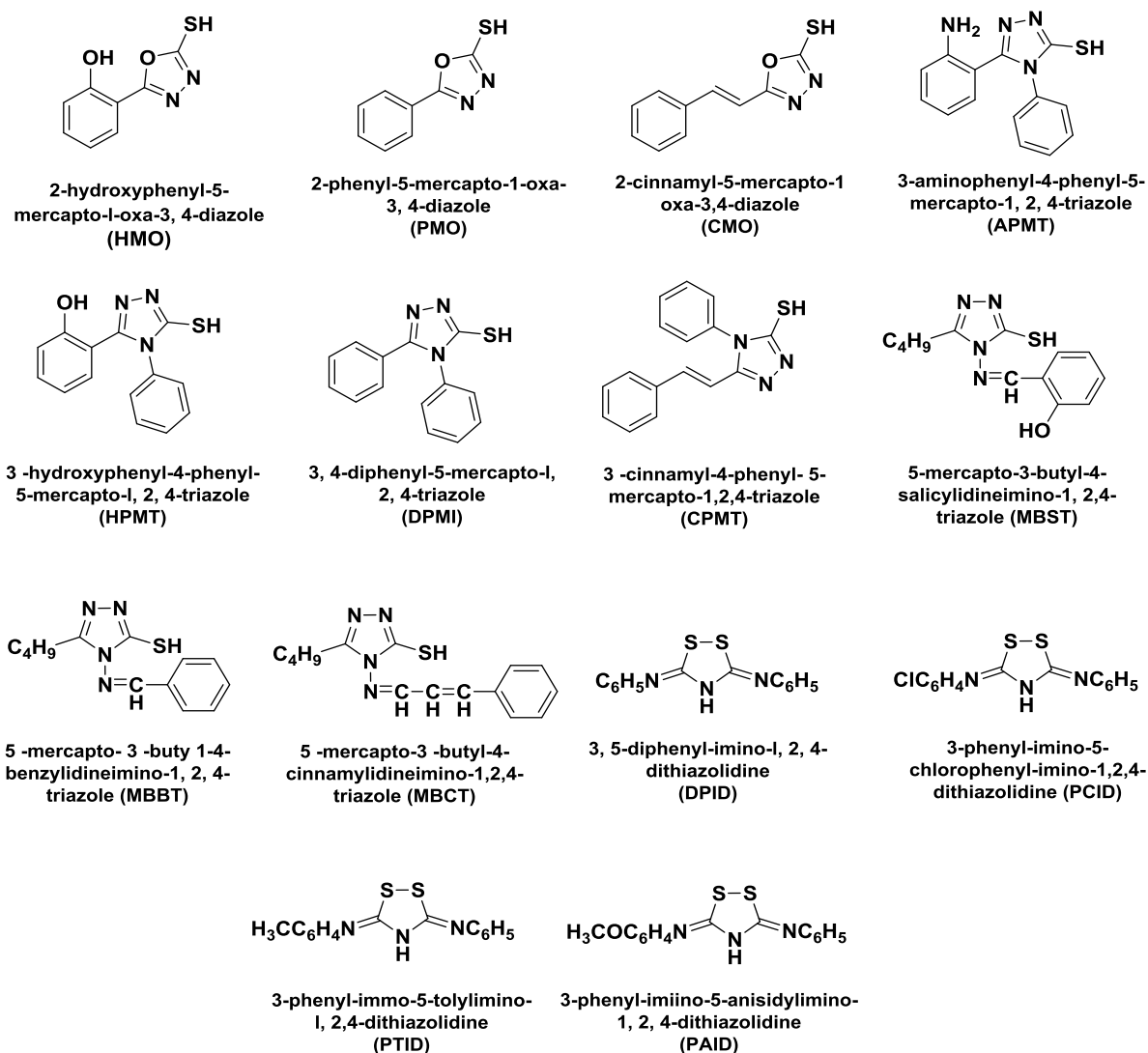


Chart 1 Classification of Inhibitors.

process obeys the Langmuir adsorption isotherm. The authors confirmed that the inhibitor molecule from protective film over steel surface via adsorption process through the π -electron density and nitrogen atoms. Quantum chemical calculations were widely studied for heterocyclic compounds to confirm whether the inhibitor molecules act as electron acceptor when they interact with steel surfaces.^[23] Yadav et al.,^[24] showed that benzimidazole derivatives exhibited good inhibition efficiencies for the corrosion of mild steel in 15 % HCl solution. The benzimidazole investigated acted as mixed type corrosion inhibitors, affecting both anodic as well as cathodic reactions. An increase the concentration of inhibitors suggested predominant anodic control over the reaction.^[24] However, the inhibition mechanism still remains unclear. In general, the inhibitors are classified into two major categories, organic and inorganic inhibitors (Chart 1). Based on the inhibition mode, the organic inhibitors are differentiated as two types, cathodic and anodic inhibitors. Alike, the inorganic inhibitors are adoption type via

Fig. 1. Molecular structures of heterocyclic compounds reported as efficient inhibitors for the corrosion of mild steel in 1 M HCl and 1 M H₂SO₄.^[25]

physical or chemical or both physical-chemical interactions. The aim of the present review is to highlight the recent work carried out using heterocyclic compounds and its derivatives for steel protection in different corrosive environments. In addition, heterocyclic compounds reported for the corrosion inhibition of steel in CO₂ saturated brine environment are also highlighted. Detail mechanisms involved in the inhibition processes are also discussed.

2. Heterocyclic Compounds Containing S, N and O atoms

So far, numerous heterocyclic compounds are reported as efficient corrosion inhibitors for the mild steel in acidic medium (1 M HCl and H₂SO₄). Very interestingly, the heterocyclic compounds that contain all the three N, O and S atoms are used as corrosion inhibitors for mild steel in acidic environments. The corrosion inhibition study includes three major methods such as weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy. Sardar et al.,^[25] prepared various heterocyclic compounds for inhibition of mild steel corrosion in acidic media. Fig. 1. Molecular structures of heterocyclic compounds reported as efficient inhibitors for the corrosion of mild steel in 1 M HCl and 1 M H₂SO₄. The reported compounds (aromatic oxadiazoles, aromatic triazoles, mercapto triazole, aromatic aldehydes, substituted dithiazolidines and substituted thiazolidines) are highly efficient towards the protection of mild steel from aggressive environments. Among various compounds tested, aromatic triazole derivatives are proved to show better inhibition efficiency than aromatic oxadiazole derivatives. It is due the presence of an additional benzene ring and 3 nitrogen atoms in triazoles when compare to the superior performance of triazoles as compared to two hetero atoms (O and N) contained oxadiazoles. The inhibitions efficiency of aromatic oxadiazoles followed the order CMO > PMO > HMO and the inhibition efficiency of aromatic triazoles followed the order CPMT > DPMT > APMT > HPMT. The high performance of CPMT is due to the presence of an additional n - bond between carbon atom (- C = C -) in conjugation with aromatic ring. The presence of delocalised n-electrons favours a greater adsorption on the metal surface thereby giving very high values of IE of > 99% even at 500 ppm concentration of inhibitor. Similarly, among mercapto triazole with different aromatic aldehydes, MBCT showed better results (MBCT > MBBT > MBST). The presence of an additional - C = C - bond in conjugation with azomethine (- C = N -) group is the main reason for its better IE values. Similarly, the IE values of substituted dithiazolidines (PAID, PTID, PCID and DPID) at 500 ppm concentration in 1M HCl and 1M H₂SO₄ followed the order; PAID > PTID > PCID > DPID. This is may be due to the fact that the presence of methoxy group (- OCH₃) which increases the density of electrons at N-atoms caused by resonance effect, which could assists the inhibitor molecules to adsorb strongly on the metal surface.

The thermodynamic parameters of all the compounds (Fig. 1), free energy of adsorption (G_{ads}), value showed low and negative value at different temperatures (30°C-50°C), indicate the spontaneous adsorption of inhibitors on the surface of mild steel in 1M HCl and 1M H₂SO₄. The adsorption behaviour of all the organic molecules on the mild steel surface obeys Langmuir's adsorption isotherm. The potentiodynamic polatization studies confirm that the

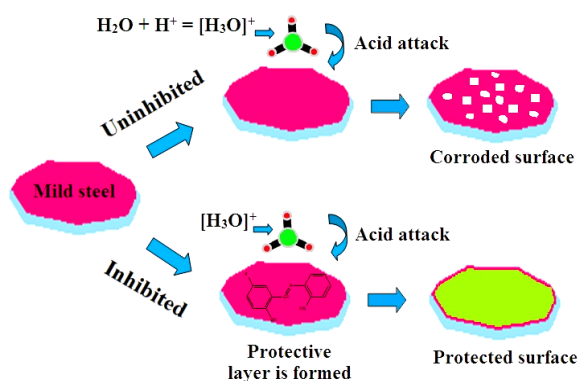


Fig. 2. Possible mechanism of corrosion inhibition of mild steel in acidic medium.^[26]

all compounds in both 1 M HCl and 1 M H₂SO₄ is mixed type inhibitors except oxadiazoles showed predominantly cathodic behaviour. However, the DPID, PCID, PTID and PAID behave predominantly anodic in 1 M H₂SO₄. The adsorption of inhibitor molecules on the metal surface occurred through heteroatoms such as N, S, O and Cl atom.

3. Corrosion Inhibition Mechanism

The inhibition mechanism for mild steel corrosion was proposed (Fig. 2). According to Saha et al.,^[26] under the acidic environment, the mild steel can be highly corroded to the metal dissolution in aggressive acid medium. Therefore, the corroded metal surface has a large number of cracks and pits. However, the inhibited mild steel surface shows very smooth morphology due to the formation of protective layer over the mild steel surface. The adsorption of heteroatoms such as N, S, O and Cl of inhibitor molecules on the metal surface is also the main reason.

According to Musa et al.,^[27] there are two possible routes for the adsorption process of heterocyclic compounds on mild steel surface; (1) forces of interactions, of the donor acceptor, between the empty d-orbitals that are present on the surface of mild steel and pi-electrons of the heterocyclic compound, and (2) inhibitor adsorption process through the forces of interactions with the Cl⁻ ions that are already adsorbed. In general, inhibition activity of heteroatom follows the reverse order of electronegativity; the inhibition performance followed in the order of: O < N < S < P. In addition, the addition of heterocyclic compounds in the acidic solutions commonly alters the electrochemical behavior or decreases the aggressiveness of the acidic environments. Interestingly, the heterocyclic compounds have sulfur (S), phosphorus (P), nitrogen (N) or oxygen (O) heteroatom effectively take part in adsorption process to protect the metals.

To further, organic molecules can adsorbed on metal surface by any one of the following mechanisms: (a) electrostatic interaction between charged surface of the metal and charge inhibitor molecule, (b) interaction of unshared electron pairs in the inhibitor molecule with the metal, (c) interaction of p-electron with metal and (d) a combination of (a) and (c) types.^[28-31] Adsorption of inhibitor molecules on metal surfaces also depend on the physico-chemical properties such as functional groups, steric factor, aromaticity,

electron density at the donor atoms and π orbital character of donating electrons and electronic structure of the molecules. Adsorption can be described by two main types of interactions such as physisorption and chemisorptions. Physisorption involves electrostatic interactions between ionic charges or dipoles on the adsorbed species and the electric charge at metal or solution interface. The heat of adsorption is low and therefore this type of adsorption is stable at low temperature. Chemisorption involves charge sharing or charge transfer from the inhibitor molecules to the metal surface and it form a coordinate type bond. It is much stronger adsorption energy than physical adsorption and also more stable at higher temperatures.^[32]

4. Corrosion in Saturated CO₂-Brine Environments

In the petroleum industries, one of the most frequent and aggressive environment is fluid with high concentration of chlorides and CO₂ which leads to CO₂ corrosion in petroleum and oil industry pipeline. Different parameters which influenced CO₂ corrosion process including pH, temperature, pressure, flow regime, steel composition, brine chemical composition and the nature of the surface films etc. When CO₂ dissolves in brine solution, it forms carbonic acid which can act as a corrosive medium on mild steel pipeline. The pH of the resulting aqueous water phase varies and it depends on the water mole fraction and other contaminants (H₂S, SO₃, NO₃⁻) present with the CO₂.^[33]

The aqueous phase dissolution of gaseous CO₂ as follows:



For above reactions, the aqueous phase pH comes approximately to 3.1, under these conditions the cathodic reactions may occur either by direct reduction of hydrogen ions or via carbonates as follows.



Also the anodic reaction as follows



Oxides may form either via one-stage reaction with carbonates, or via two stage reaction with bicarbonates.



In general, CO₂ corrosion occurs in anaerobic (oxygen free) condition, because the oxidation of ferrous to ferric has not yet been reported. So CO₂ corrosion is also referred to as acid corrosion, due

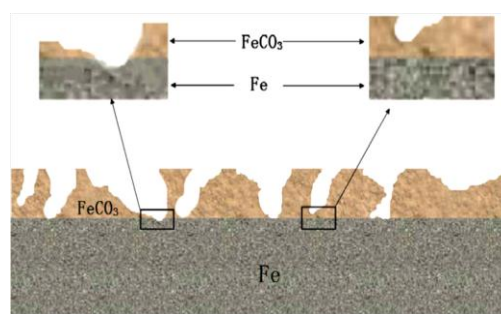


Fig. 3. Sketch of corroded mild steel surface in CO₂ environment ^[32].

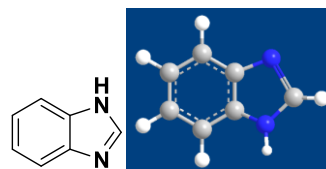
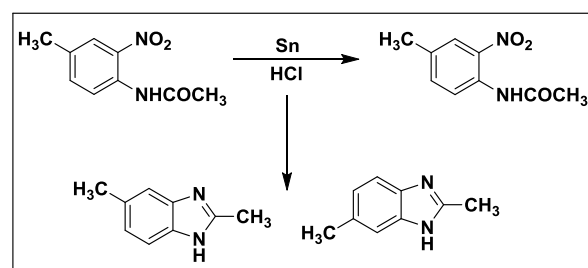


Fig. 4. Molecular structure of benzimidazole.



Scheme 1. Synthesis of benzimidazole derivatives. ^[40]

to the formation of weak carbonic acid and release of hydrogen ion (H⁺).^[34-36] In CO₂ saturated environment, the major corrosion product formed on metal surface is FeCO₃, which is deposited on Fe surface to form loose and porous layer,^[37-39] as shown in Fig. 3.

5. Benzimidazole and its Derivatives

Benzimidazole derivatives have attracted significant attention for mild steel corrosion inhibition in acidic environment for the past two decades. It is a heterocyclic aromatic organic compound with a bicyclic structure comprising a phenyl ring fused to an imidazole ring, the molecular structure of benzimidazole is given in Fig.4.

The first benzimidazole derivative was prepared in 1872 by Hoebrecker. He obtained 2,6-dimethylbenzimidazole by the reduction of 2-nitro-4-acetanilide ^[40] (Scheme 1). The ring possesses a high degree of stability also it is not affected by concentrated sulphuric acid, hot hydrochloric acid as well as alkalis. The melting point of benzimidazole derivatives is general lower with the introduction of substituent into 1-position. Benzimidazoles with imide nitrogen are soluble in polar solvents and less soluble in organic solvents. Introduction of non-polar substituents in various position of benzimidazole ring will enhance the solubility in non-polar solvents. Benzimidazoles are weakly basic in nature, also less basic than imidazoles and are soluble in dilute acids and it also soluble in aqueous alkali and form N-metallic compounds.^[41-43]

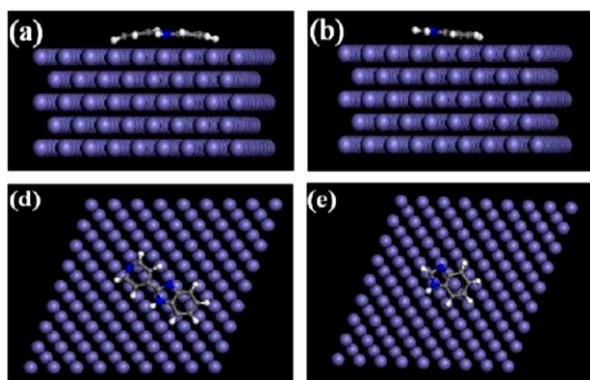


Fig. 5. Equilibrium adsorption configuration of benzimidazoles.^[45]

Roque et al.,^[44] documented the use of benzimidazole derivatives as efficient corrosion inhibitor for carbon steel surface by density functional theory (DFT) and electrochemical measurements. DFT and electrochemical results clearly shows that the benzimidazole derivatives adsorbed over the metal surface by giving the π -electron density from delocalised region ($N=C=N$) through its highest occupied molecular orbital (HOMO) to the metal lowest un-occupied molecular orbital (LUMO). Inhibition performance of 2-(4-pyridyl)-benzimidazole against mild steel corrosion in hydrochloric acid medium were studied by Zhang et al.^[45] The benzimidazole derivative showed mixed type inhibition and its adsorption process obeys Langmuir adsorption isotherm. Molecular dynamics simulation reveals that the benzimidazole derivatives adsorb on metal surface in the flat manner. The interactions between the inhibitor molecule and iron surface as well as best adsorption configurations for the benzimidazole and its derivatives were simulated using molecular dynamic simulations as given in Fig. 5.

Corrosion causes serious issues and more economical drawbacks in oil gas industries worldwide. In oil and gas pipelines, the carbon dioxide (CO_2) environment creates corrosion products on the surface of the pipelines. To solve this issue, many organic inhibitors were developed which creates a protective film on steel surface. Organic corrosion inhibitors have been successfully used for several internal corrosion of carbon steel construction in oil and gas industry.

Benzimidazole derivatives are very simple and N-containing heterocyclic organic compound extensively used as corrosion inhibitors for steel in various environments. The efficiency of benzimidazole derivatives depend on the nature of hydrocarbon or substituent groups attached to the carbon or nitrogen atoms of the benzimidazole ring. Benzimidazole derivatives are usually adsorbed on metal surface forming a protective layer that interfaces with the electrochemical reactions involved in the corrosion process. Heydari and Javidi^[46] reported on the corrosion inhibition and adsorption behaviour of an amido-imidazoline derivative (IM) on API 5L X52 steel in saturated CO_2 with 3 wt% NaCl environment and further investigated on synergistic effect of iodide ions by using electrochemical measurements and surface analysis. Electrochemical measurements revealed that the inhibition efficiency was concentration dependant and it increased with increase in concentration of inhibitor. Potentiodynamic polarization measurements show that the IM functioning as a mixed type inhibition (anodic and cathodic behaviour). For the synergistic effect,

the addition of iodide ions with IM enhances the corrosion inhibition efficiency and the synergism parameter was greater than unity. IM adsorption process on mild steel was followed by Langmuir adsorption isotherm. Further, the values of Gibbs free energy of adsorption concluded that IM was chemically adsorbed on mild steel surface.^[46]

Sheng et al.,^[47] reported that 2-methylbenzimidazole (MBI) potentially inhibited mild steel corrosion in sterile enriched artificial sea water with sulphate reducing bacteria medium. Inhibitor MBI strongly reduces the cathodic current density which adsorbed on mild steel surface and acted as cathodic inhibitor. By retarding the transfer of hydrogen and chloride from the bulk solution to the mild steel or solution interface, its adsorption on mild steel surface and obeys Langmuir adsorption isotherm. Cao et al.,^[48] showed that some structurally similar benzimidazole molecules showed similar ability to donate the electrons while the difference in inhibition performance should mainly be attributed to the difference in accepting electrons. Adsorption behaviour and accepting electrons of benzimidazole derivatives such as 2-aminomethyl benzimidazole (ABI), bis(2-benzimidazolylmethyl)amine (BBIA) and tri-(2-benzimidazolylmethyl)amine (TBIA) were compared and results obey the order of $TBIA > BBIA > ABI$. Results also showed that ABI and BBIA adsorbed on the metal surface in an almost horizontal orientation in aqueous solution while one of the benzimidazole segments of TBIA showed a tilted orientation on metal surface.

Niamien et al.,^[49] showed that benzimidazole derivatives have superior corrosion inhibition efficiency of copper in 1 M HNO_3 medium. The inhibition efficiencies were investigated experimentally and theoretically. Results indicate that the inhibition efficiencies increase with increasing temperature and increasing concentration of inhibitors. The adsorption of inhibitors on metal surface obeyed the modified Langmuir adsorption isotherm. The 1,4-bis-benzimidazolyl-butane (BBB) was investigated as a potential corrosion inhibition for mild steel in 0.5 M hydrochloric acid medium.^[50] Corrosion inhibition efficiencies were studied by electrochemical measurements and surface analysis. Quantum chemical calculations and atomic force microscopy images were additionally applied to reveal the adsorption structure and confirmed the experimental results.

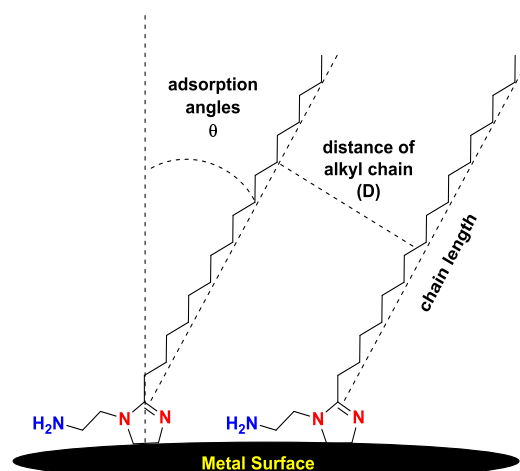


Fig. 6. The schematic representation of adsorption angle and distance of alkyl chain.^[53]

Table 1 Benzimidazole derivatives.

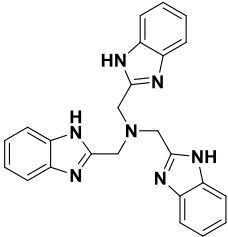
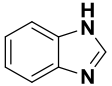
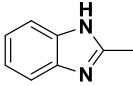
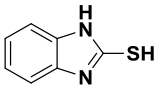
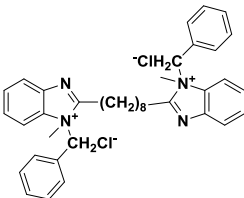
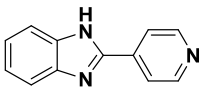
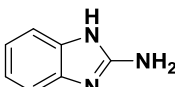
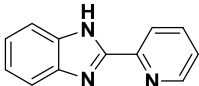
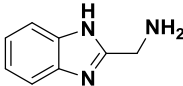
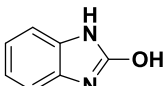
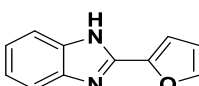
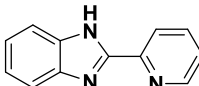
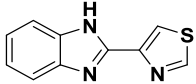
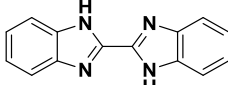
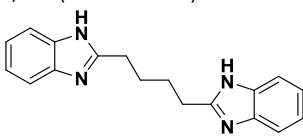
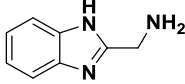
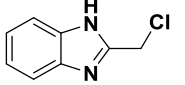
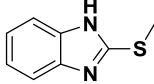
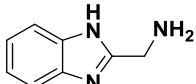
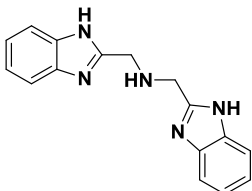
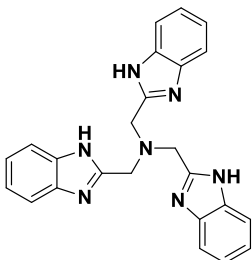
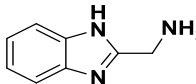
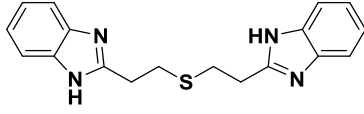
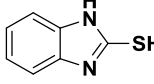
S. No	Structure and name of benzimidazole derivative	Metal	Conc. of INH	Medium	EIS	Isotherm	Ref.
1	 Tris(benzimidazole-2-ylmethyl)amine	Mild steel	0.07 mM	1.0 M HCl	80.0	-	[57]
2	 Benzimidazole	Mild steel	250 ppm	1.0 M HCl	73.8	Langmuir	[58]
3	 2-methylbenzimidazole	Mild steel	250 ppm	1.0 M HCl	76.3	Langmuir	[58]
4	 2-mercaptobenzimidazole	Mild steel	250 ppm	1.0 M HCl	90.4	Langmuir	[58]
5	 1,8-bis(1-chlorobenzyl-benzimidazolyl)-octane	Mild steel	130 μ M	1.0 M HCl	99.1	Langmuir	[59]
6	 2-(4-pyridyl)-benzimidazole	Mild steel	2.0 mM	1.0 M HCl	82.1	Langmuir	[45]
7	 2-aminobenzimidazole	Iron	50 mM	1.0 M HCl	76.0	Langmuir	[60]
8	 2-(2-pyridyl)benzimidazole	Iron	50 mM	1.0 M HCl	72.4	Langmuir	[60]
9	 2-aminomethylbenzimidazole	Iron	50 mM	1.0 M HCl	62.3	Langmuir	[60]
10	 2-hydroxybenzimidazole	Iron	50 mM	1.0 M HCl	57.1	Langmuir	[60]
11	 2-(2-furanyl)-1H-benzimidazole	Iron	0.2 mM	1.0 M HNO ₃	76.3	-	[56]
12	 2-(2-pyridyl) benzimidazole	Iron	0.2 mM	1.0 M HNO ₃	86.4	-	[61]

Table1 continues.

13		Iron	0.2 mM	1.0 M HNO ₃	96.8	-	[61]
	2-(4-thiazolyl) benzimidazole						
14		Mild steel	1 mM	1.0 M HCl	-	Langmuir	[62]
	2,2-bis(benzimidazole)						
15		Mild steel	.068 mM	0.5 M HCl	98.1	Langmuir	[63]
	1, 4-bis-benzimidazolyl-butane						
16		Iron	0.2 mM	1.0 MHNO ₃	75.2	-	[63]
	2-(aminomethyl)benzimidazole						
17		Iron	0.2 mM	1.0 MHNO ₃	87.1	-	[64]
	2-(chloromethyl)benzimidazole						
18		Iron	0.2 mM	1.0 MHNO ₃	93.8	-	[64]
	2-(methylthio)benzimidazole						
19		Mild steel	2.0 mM	1.0 M HCl	72.2	Langmuir	[48]
	2-aminomethyl benzimidazole						
20		Mild steel	2.0 mM	1.0 M HCl	91.8	Langmuir	[48]
	bis(2-benzimidazolylmethyl) amine						
21		Mild steel	2.0 mM	1.0 M HCl	92.0	Langmuir	[48]
	tri(2-benzimidazolylmethyl) amine						
22		Mild steel	1.0 mM	0.5 M HCl	82.0	-	[65]
	2-aminomethylbenzimidazole						
23		Mild steel	1.0 mM	0.5 M HCl	95.6	-	[65]
	bis(benzimidazol-2-ylethyl)sulfide						
24		Mild steel	1.0 mM	1.0 M HCl	95	Langmuir	[66]
	2-Mercapto benzimidazole						

Abboud et al.,^[51] documented that 500 μM concentration of 2-(*o*-hydroxyphenyl)benzimidazole (HPB) shows 93% corrosion inhibition efficiency on mild steel in 1 M hydrochloric acid medium. Electrochemical measurement describes HPB acts anodic and cathodic inhibition with predominance of anodic character. X-ray diffraction pattern clearly revealed that the inhibitor molecules form protective film on the mild steel surface. The corrosion inhibition of iron in 1.0 M nitric acid by some benzimidazole derivatives such as 2-(aminomethyl)benzimidazole (AB), 2-(chloromethyl)benzimidazole (CB) and 2-(methylthio) benzimidazole (MB) showed their potential corrosion inhibition efficiencies. Inhibitory properties of benzimidazole derivatives were confirmed by density functional theory and the results showed that aminomethyl group present in AB is responsible for its enhanced corrosion inhibition efficiency.^[52]

Zhang et al.,^[53] reported on the corrosion inhibition mechanism and molecular modelling of 1-(2-aminoethyl)-2-alkyl-imidazoline derivatives for carbon steel against CO_2 corrosion. Quantum chemical and experimental results showed that with increase of alkyl length, interaction between inhibitor molecule and metal surface was enhanced. The schematic representation of adsorption angle and distance of alkyl chain is given in Fig. 6.

Adsorption and corrosion inhibition property of benzimidazole derivatives such as benzimidazole, 2-methylbenzimidazole, 2-hydroxymethylbenzimidazole, 2-aminobenzimidazole, 2-mercaptobenzimidazole, 5(6)-nitrobenzimidazole, 5(6)-carboxybenzimidazole and 2-benzimidazolylacetonitrile in 1.0 M HCl solution was investigated by Popova et al.^[54] Gravimetric measurement results showed that the maximum inhibition efficiency of 94.0 % and 94.7 % was achieved at 10⁻³ M concentration of 2-benzimidazolylacetonitrile and 2-mercaptobenzimidazole respectively. The 5(6)-carboxybenzimidazole follows Langmuir adsorption isotherm and other derivatives follows Frumkin isotherm. Villamizar et al.,^[55] studied the corrosion inhibition efficiency of carbon steel with imidazolium derivatives in 3 % NaCl with and without diesel saturated with CO_2 at 50°C. Results showed that in the presence of diesel, imidazolium derivatives showed higher corrosion inhibition efficiency.

Popova et al.,^[54] studied effect of temperature on mild steel corrosion in acidic media in the presence of benzimidazole derivatives namely 2-Aminobenzimidazole, 2-Mercaptobenzimidazole, 1-Benzylbenzimidazole and 1,2-Dibenzylbenzimidazole. The room temperature inhibitors 2-Mercaptobenzimidazole, 1-Benzylbenzimidazole and 1,2-Dibenzylbenzimidazole showed good inhibition efficiencies at 97%, 98% and 98.2% respectively. Increase in temperature resulted in the decrease of corrosion inhibition efficiency of benzimidazole derivatives. This was reported to be due to the value of the apparent activation energy (E_a) in inhibited solution being greater than that in uninhibited solution. However, 1-Benzylbenzimidazole showed slightly increase in inhibition efficiency at higher temperature, which is due to the value of E_a for the corrosion process is smaller than that obtained in the uninhibited solution. This is an indication, according to the authors, for a specific type of adsorption of the inhibitor.^[54-56]

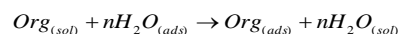
Corrosion inhibition efficiency and adsorption phenomenon of benzimidazole derivatives on steel surfaces in acidic environment are summarised in Table 1.

Recently, a synergistic effect of 2-mercapto benzimidazole with iodide ions was studied by Zhang et al.^[67] The synergistic effect was attributed to the adsorption of iodide anions on the copper surface, which facilitated the adsorption of protonated 2-mercapto benzimidazole and the formation of an inhibitive film. Results showed 74.2 % corrosion inhibition efficiency towards the corrosion of copper surface in 0.5 M sulphuric acid solution. However, with the addition of 0.25 mM of potassium iodide into the inhibitor solution, the inhibition efficiency increased to 95.3 %.

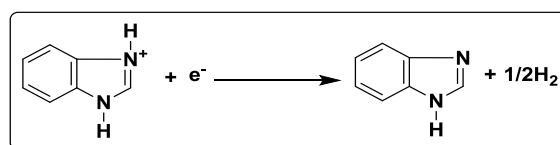
Obot et al.,^[68] documented the theoretical studies of benzimidazole, 2-methylbenzimidazole and 2-mercaptobenzimidazole in 1.0 M HCl medium. Density functional theory quantum chemical calculations were used to explain the electronic structure of benzimidazole derivatives and their potential to inhibit the corrosion of mild steel were explained.

5.1. Corrosion Inhibition of Benzimidazole in Acidic Environments

Benzimidazole based corrosion inhibitors possess two anchoring sites suitable for bonding on steel surfaces: the nitrogen atom with its lonely sp^2 electron pair and the aromatic rings. They can adsorb on the steel surface in the form of (i) a neutral molecule via chemisorptions mechanism, involves the sharing of electrons between the nitrogen atom and steel surface, (ii) adsorption can also occur through p-electron interactions between the benzimidazole ring of the molecule and the steel surface and (iii) cationic form with positively charged part (ammonium-N) of the molecule oriented toward negatively charged steel surface.^[60-69,70] In general, the corrosion inhibition efficiency of an inhibitor depends on its adsorption on metal surface, which consist of replacement of water molecule by the organic inhibitor at the interface as follows.^[70]



The inhibitor molecule adsorption depends on certain physico-chemical properties such as functional groups, steric factors, aromaticity, electron density at the donor atoms, p-orbital character of donating electrons and the electronic structure of inhibitor molecules, etc.^[71-73] The corrosion inhibition efficiency varies with substituent groups and substituent position on benzimidazole ring. In general, benzimidazole derivatives protect corrosion inhibition on steel follows acid-base interactions. Based on this concept, benzimidazole would act as a strong base, which can serve as an electron donor. On other hand, Fe^{3+} , Fe^{2+} and Fe would behave as Lewis acids or electron acceptors.



Scheme 2 Cation form of benzimidazole reduced to neutral molecule.^[34]

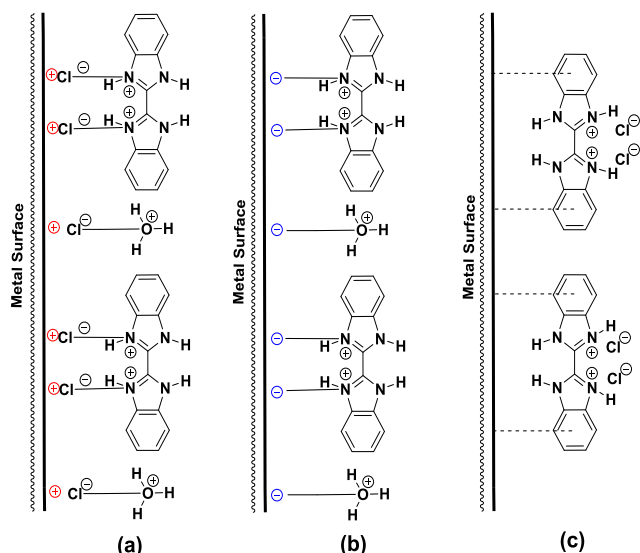


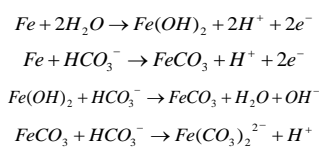
Fig. 7. Schematic representation of adsorption behaviour of benzimidazole derivatives on mild steel in acid solution: (a) mild steel surface with positive charge, (b) mild steel surface with negative charge and (c) mild steel surface at potential of zero charge.^[62]

Lopez et al.,^[34] studied the corrosion inhibition efficiency of benzimidazole on steel surface in deoxygenated of 5 % sodium chloride solution with saturated CO₂ medium and further discussed the influence of steel microstructures such as quenched and tempered. The protective action of benzimidazole ring was explained by the formation of metal-inhibitor bond and its ring can acts as a strong base. In the acidic environments, benzimidazole ring was protonated and it acts as cations. Protonated benzimidazole shows increased charge redistribution on imidazole and benzene rings, this support the inhibitor metal bond formation. Further it was reduced to neutral molecule on the cation surface as follows (Scheme 2).

Benzimidazole derivatives have been shown to adsorbed on metal surface through electrostatic interaction between the positively charged nitrogen atoms and negatively charged metal. In addition to that the aromatic ring, π -electron interaction between the aromatic nucleus and the positively charged metal surface also interact.^[62-74] The clear representation of metal and benzimidazole derivative interaction is given in Fig.7.

5.2. Corrosion Inhibition of Benzimidazole in Saturated CO₂-Brine Environment

Veawabet al.,^[75] reported that dissolved CO₂ is a primary corroding agent in alkanolamine gas plants. Burstein and Davies^[76] proposed the mechanism for metal dissolution in bicarbonate solution as follows.



Imidazolines with longer aliphatic chains showing hydrophilic and hydrophobic nature have been investigated as CO₂ corrosion inhibitors. These hydrophobic properties have been associated with

the formation of protective film on steel surface and thereby drastically reducing steel corrosion process.^[55- 77]

Wang et al.,^[78] studied the corrosion inhibition efficiency of thioureidoimidazoline (TAI) on Q235 steel by electrochemical measurements, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). TAI molecules adsorbed on steel surface through chemisorbed film on metallic surface which occurred by the formation of coordination bonds between hetero atoms in the TAI molecule and Fe on the metallic surface, as was demonstrated by XPS and AFM analysis of the tested surface.

Corrosion inhibition efficiency of ethylaminoimidazoline derivatives on mild steel surface in CO₂ saturated 3% NaCl environment was studied by Okafor et al.^[79] Inhibition efficiency was calculated by electrochemical measurements as well as SEM observations. Further investigation of the effects of iodide ion on the inhibition efficiency of imidazoline derivatives in mild steel specimens were investigated in 3% NaCl + 80 mg/l inhibitor + 2000 mg/l KI. After 3 h of immersion the maximum inhibition efficiency at 97.3 % were obtained.

Heydari et al.,^[80] reported the corrosion inhibition and adsorption behaviour of an amido-imidazoline derivative (IM) on API 5L X52 steel in CO₂-saturated 3% NaCl solution and synergistic effect of iodide ions. The corrosion inhibition efficiency was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Results showed maximum inhibition efficiency of 94.3 % was achieved at 100 IM mg/l + 2000 KI. Electrochemical investigations revealed that 1M showed mixed type corrosion inhibition and its adsorption process follows Langmuir adsorption isotherm which is through the chemisorption as well as physisorption occurring on metal surface.

Microstructures (annealed, and quenched and tempered) of mild steel plays an important role on corrosion in saturated CO₂ environment. Lopez et al.^[81] reported the benzimidazole served as corrosion inhibitor with the concentration of 100 ppm at different microstructures of mild steel. On an annealed sample surface, benzimidazole shows potential corrosion inhibition efficiency. Corrosion inhibition mechanism follows the reduction of protonated species at cathodic sites (Fe₃C), leading to the adsorption and blockage of these active areas which delays the FeCO₃ precipitation.^[34, 81]

6. Triazole Heterocyclic Compounds

There are several five membered heterocyclic compounds have been studied for the corrosion inhibition of Fe-steel and alloys. In particular, 1,2,4-triazole and 1,2,3-triazole are widely studied as corrosion inhibitors for the Fe-steel (Fig. 8). In addition to the excellent coordination ability, the triazole-based compounds are eco-friendly, cost-effective, easily synthesizable, and operative at low

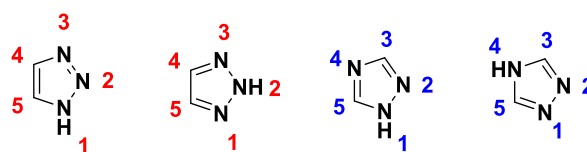
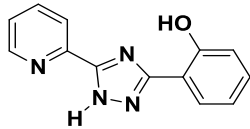
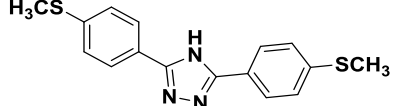
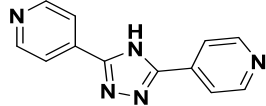
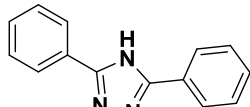
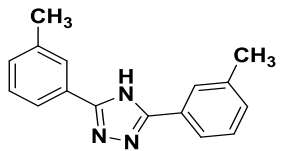
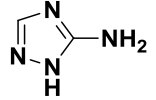
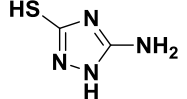
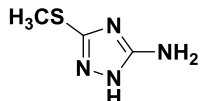
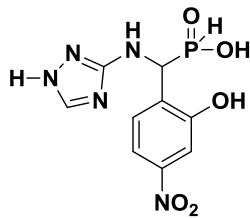
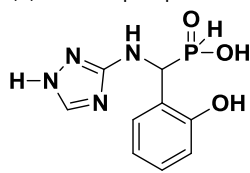
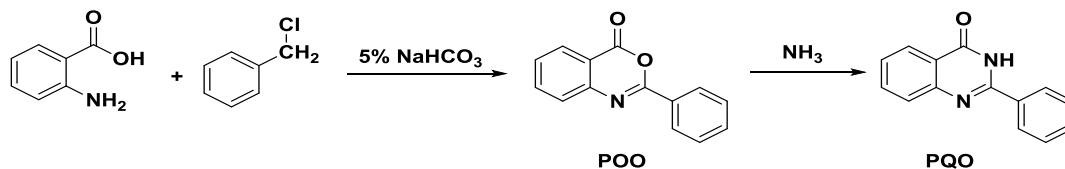


Fig. 8. Structure of 1,2,3-triazole and 1,2,4-triazole heterocyclic compounds

Table 2 Heterocyclic 1,2,4-triazole derivatives.

S. No	Molecular Structure and name of Inhibitor	Medium	Type of INH	Conc. of INH	Maximum IE (%)	Ref.
1	 2[5-(2-Pyridyl)-1,2,4-triazol-3-yl]phenol	1 M HCl	Mixed	80 mg/L	89.9 %	[82]
2	 3,5-Bis(4-methylthiophenyl)-4H-1,2,4-triazole	1 M HCl	Mixed	5×10^{-4} m	96.8 %	[83]
3	 3,5-Bis(4-pyridyl)-4H-1,2,4-triazole	1 M HCl	Mixed	5×10^{-4} m	95.5 %	[83]
4	 3,5-Diphenyl-4H-1,2,4-triazole	1 M HCl	Mixed	5×10^{-4} m	89.1 %	[84]
5	 3,5-Di(m-tolyl)-4-amino-1,2,4-triazole	1 M HCl	Mixed	5×10^{-4} m	82.8 %	[85]
6	 5-Amino-1,2,4-triazole	0.1 M HCl	Cathodic	1×10^{-2} m	24 %	[86, 6-A]
7	 5-Amino-3-mercapto-1,2,4-triazole	0.1 M HCl	Mixed	2×10^{-3} m	90 %	[86]
8	 5-Amino-3-methyl thio-1,2,4-triazole	0.1 M HCl	Mixed	1×10^{-2} m	82 %	[86]
9	 3-p-Nitro-benzylidene amino-1,2,4-triazole phosphonate	Neutral aqueous solution	Mixed	4 ppm	63 %	[87]
10	 3-Salicylalidene amino-1,2,4-triazole phosphonate	Neutral aqueous solution	Mixed	5 ppm	57 %	[87]

INH – inhibitor; Ref- Reference



Scheme 3. Synthesis of benzofused heterocyclic compounds, 2-phenylquinazolin-4(3H)-one (PQO) and 2-phenyl-4H-benzo[d]oxazin-4-one (POO).^[88]

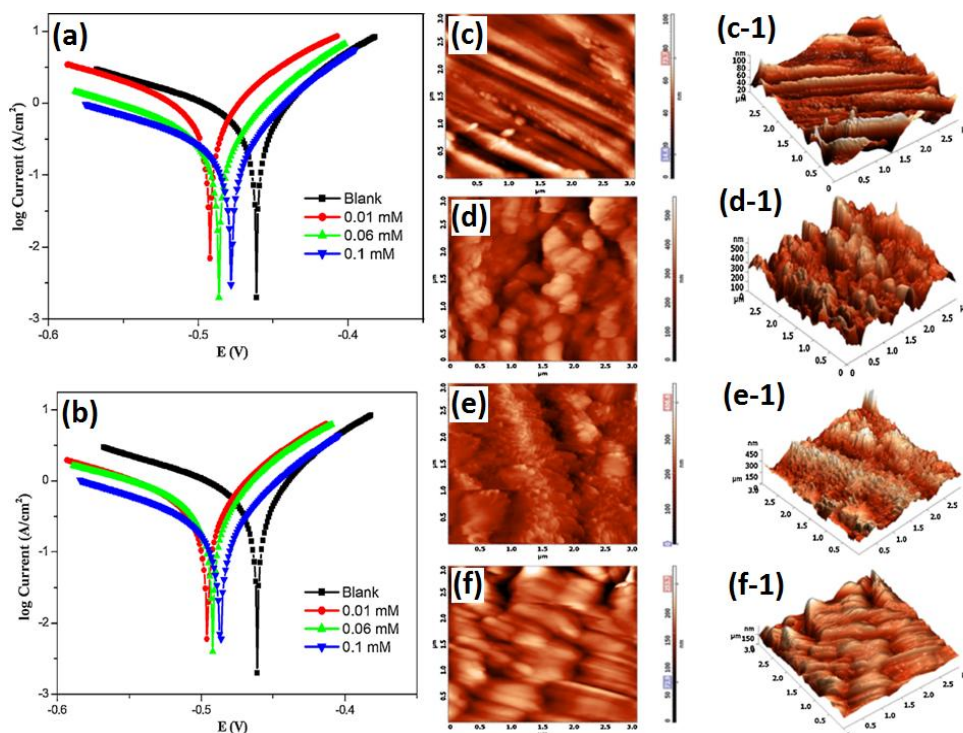


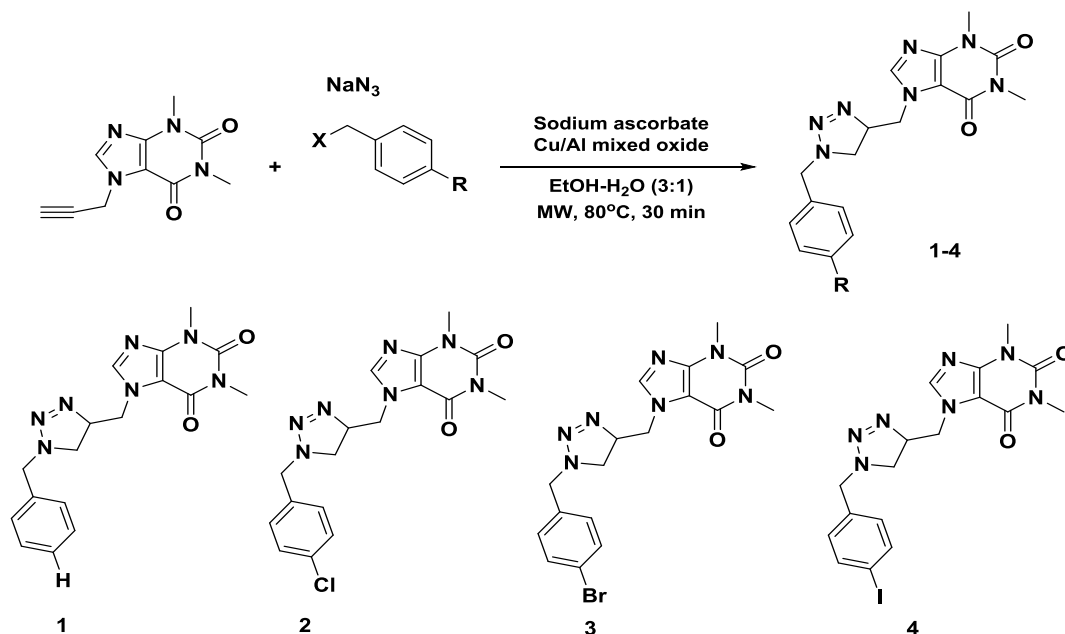
Fig. 9. Potentiodynamic polarization curves for mild steel in 1 M H_2SO_4 in presence and absence of (a) POO and (b) PQO. AFM topography of mild steel (c, c-1) polished, (d, d-1) uninhibited, inhibited by (e, e-1) POO, and (f, f-1) PQO.^[88]

concentrations. The presence of various functional groups and electron donating atoms are the advantages of the 1,2,4-triazole, 1,2,3-triazole and its derivatives. The activity of 1,2,4-triazole, 1,2,3-triazole derivatives was found to be moderate in the neutral conditions. Corrosion inhibition efficiency and adsorption phenomenon of 1,2,4-triazole and 1,2,3-triazole derivatives on steel surfaces in different environments are summarised in Table 2. For example, Bentiss et al.,^[82] prepared some 4H-triazole derivatives, namely 3,5-diphenyl-4H-1,2,4-triazole, 3,5-bis(4-pyridyl)-4H-1,2,4-triazole and 3,5-bis(4-methylphenyl)-4H-1,2,4-triazole and used as corrosion inhibitors for mild steel in 1 M HCl. Weight loss, ac impedance measurements and polarisation curves were performed to evaluate the inhibitive action of the reported compounds. Electrochemical measurements revealed that the inhibitors are mixed type in nature. The IE values increase with the concentration of inhibitors and the maximum IE of 99.6 % was achieved for the 4-MTHT at 5×10^{-4} M.

El Mehdi and co-workers^[85] studied corrosion inhibition ability of newly prepared triazole-derivatives such as 5-di(m-tolyl)-4-amino-1,2,4-triazole (m-DTAT) and 3,5-di(m-tolyl)-4H-1,2,4-triazole (m-THT) in 1 M HCl solution. Although both the m-DTHT and m-DTAT demonstrate the excellent inhibition efficiency towards corrosion of

mild steel in 1 M HCl solution, the m-DTAT reached better inhibition efficiency of 95% whereas the m-DTHT showed 91 %. Surprisingly the electrochemical measurements showed that the m-DTHT is a mixed type in nature whereas m-DTAT is a cathodic in nature. On contrary, the adsorption of m-DTHT and m-DTAT inhibitor molecules on the mild steel surface is found to obey the Langmuir adsorption isotherm. The slight change in the IE can be explained by the availability of the pair of free electrons of the nitrogen atom, to form a donor-acceptor-type link, necessary for the formation of a protective chemisorbed film. There are some triazole-derivatives are tested as corrosion inhibitors for the mild steel under neutral conditions.^[87]

Hemapiya et al.,^[88] reported two benzofused heterocyclic compounds, namely 2-phenylquinazolin-4(3H)-one (PQO) and 2-phenyl-4H-benzo[d]oxazin-4-one (POO) (Scheme 3), for corrosion of mild steel in 1 M H_2SO_4 solution. Gravimetric and electrochemical methods were employed to study the inhibitive property. They found that the PQO showed better IE values when compare to POO. The order of inhibition efficiency follows $\text{PQO} > \text{POO}$. The better IE value of PQO is due to the additional N-atom present in the PQO. Both PQO and POO showed mixed mode of inhibition and the passive film formation on mild steel surface was confirmed by SEM-EDX. The



Scheme 4. Synthesis of 1,2,3-triazole derivatives in the presence of Cu(Al)O catalyst (1-4 1,2,3-triazole derivatives).^[89]

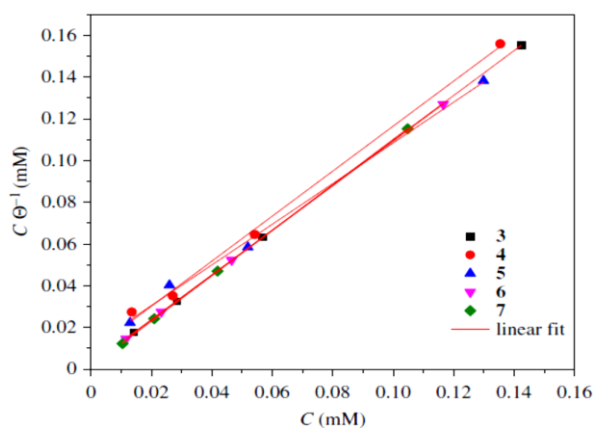


Fig. 10. Adjustment of the thermodynamic analysis of the theophylline-triazole derivatives in API 5 L X52 steel immersed in 1 M HCl by using the Langmuir model.^[89]

efficiency increases with concentration and decreases with rise in temperature. Thermodynamic parameter values confirmed the inhibitors adsorb on the mild steel surface by physisorption.

The metal surface at nano and micro level can be effectively examined by AFM analysis. Average roughness, R_a , and root-mean square roughness, R_q values obtain via AFM are very useful to understand the nature of the inhibitor or nature of inhibition. AFM has been used to investigate the formation of layers on the mild steel surface by PQO and POO molecules (Fig 9). The topography of uninhibited mild steel surface showed high roughness values, whereas, the inhibited plates showed lower values. The POO and PQO showed low R_a (52.92 nm and 34.98 nm) and R_q (70.43 nm and 44.28 nm) values for mild steel immersed in 1 M H_2SO_4 containing 0.1 mM, whereas, the unprotected mild steel showed R_q values of 102.29 nm and R_a value of 78.92 nm. The results showed the formation of protective film on mild steel surface by inhibitor molecules.

Espinoza-Vazquez and co-workers prepared a series of theophylline derivatives containing 1,2,3-triazole moieties. Scheme 4 shows the synthesis of 1,2,3-triazole derivatives using Cu(Al)O as catalyst (1-4, 1,2,3-triazole derivatives). The name of the derivatives are: 7-((1-benzyl-1H-1,2,3-triazol-4-yl) methyl)-1,3-dimethyl-3,7-dihydro-1H-purine-2,6-dione (1), 7-((1-(4-chlorobenzyl)-1H-1,2,3-triazol-4-yl) methyl)-1,3-dimethyl-3,7-dihydro-1H-purine-2,6-dione (2), 7-((1-(4-bromobenzyl)-1H-1,2,3-triazol-4-yl) methyl)-1,3-dimethyl-3,7-dihydro-1H-purine-2,6-dione (3), and 7-((1-(4-iodobenzyl)-1H-1,2,3-triazol-4-yl) methyl)-1,3-dimethyl-3,7-dihydro-1H-purine-2,6-dione (4). The synthesized derivatives are used as corrosion inhibitors for the API 5 L X52 steel in 1 M HCl medium. All the 1,2,3-triazole derivatives demonstrate an excellent inhibition efficiency towards the corrosion of the API 5 L X52 steel in 1 M HCl medium. They found that at 50 ppm concentration of inhibitors are enough to achieve the maximum inhibition efficiency. The Langmuir isotherm explain that the compounds 2 and 3 exhibit physisorption-chemisorption process, whereas the compounds 1 and 4 exhibit chemisorption process. Among the 1,2,3-triazole derivatives (1-4), the compounds 2 and 4 (bearing chlorine or iodine at the para position of the aromatic ring) have greater inhibition ability when compare to the compounds 1 and 3. Fig. 10 shows the adjustment of the thermodynamic analysis of the theophylline – triazole

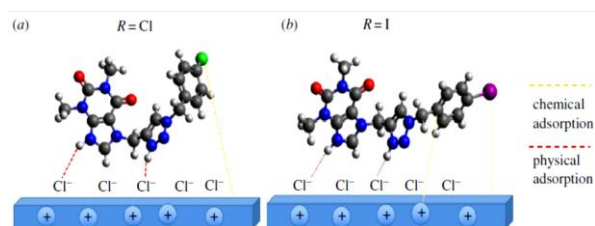


Fig. 11. Schematic of the adsorption behaviour of inhibitor on API 5 L X52 steel surface immersed in 1 M HCl.^[89]

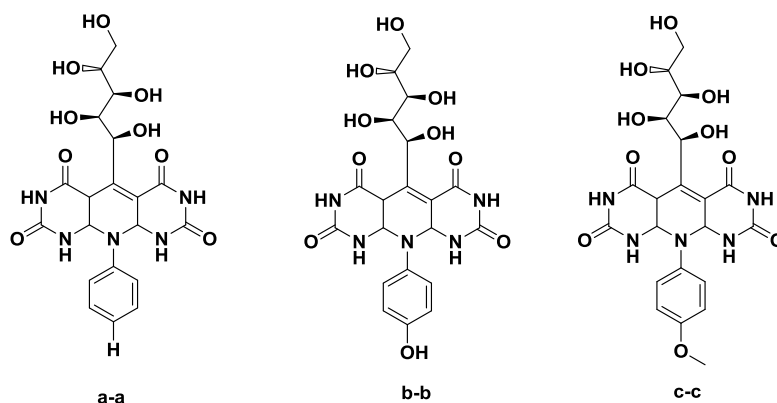
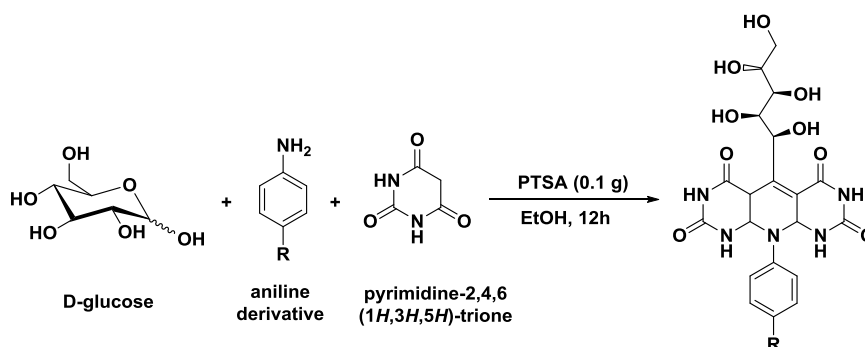


Fig. 12. Molecular structure of D-glucose derivatives of dihydropyrido-[2,3-d:6,5-d']-dipyrimidine-2, 4, 6, 8(1H,3H, 5H,7H)-tetraone (a-a = GPH-1, b-b = GPH-2, c-c = GPH-3).^[90]



Scheme 5. Synthesis of D-glucose derivatives of dihydropyrido-[2,3-d:6,5-d']-dipyrimidine-2, 4, 6, 8(1H,3H, 5H,7H)-tetraone (GPH-1, GPH-2, GPH-3).^[90]

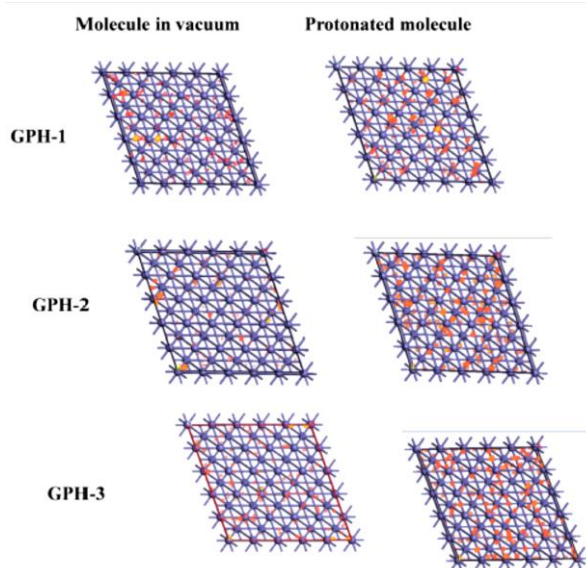


Fig. 13. Top views of the density distribution of the most stable low energy configuration for the adsorption of inhibitor molecules at Fe (110) surface obtained by Monte Carlo simulations.^[90]

derivatives for API 5 L X52 steel immersed in 1 M HCl by using the Langmuir model. Fig. 11 illustrates the mode of absorption of inhibitor molecules on the surface of API 5 L X 52 steel surfaces immersed in 1 M HCl.

D-glucose derivatives of dihydropyrido-[2,3-d:6,5-d']-dipyrimidine-2, 4, 6, 8(1H,3H, 5H,7H)-tetraone (GPH-1, GPH-2, GPH-3) (Fig. 12) have been synthesized by Verma and co-workers (Scheme 5).^[90] The GPH-1, GPH-2, GPH-3 are tested as corrosion inhibitors for the mild steel in 1M HCl. They found that the order of inhibition

efficiencies is GPH-3 > GPH-2 > GPH-1. The results showed that the electron releasing (-OH, -OCH₃) group containing inhibitors exhibit higher efficiency than the inhibitor molecule without any substituents. The inhibitors are found to be mixed type in nature (predominantly cathodic inhibitive effect) and the adsorption of GPH-1, GPH-2, and GPH-3 molecules on mild steel surface follows Langmuir isotherm. Inhibition efficiency was calculated from electrochemical results: GPH-3 (97.82%) > GPH-2 (95.21%) > GPH-1(93.91%). Fig. 13 shows the top views of the density distribution of the most stable low energy configuration for the adsorption of GPH-1, GPH-2, GPH-3 molecules at Fe (110) surface obtained by Monte Carlo simulations. Monte Carlo simulations study revealed that values of adsorption energy increased in presence of electron releasing -OH and -OCH₃ groups.

Laabaissi et al.,^[91] reported 4,5-benzodiaz-acetylmethylene-pine-2-one (AMBz) for the corrosion inhibition of carbon steel in 2.0 M phosphoric acid and 1.0 M HCl chloridric acid. Corrosion studies reveal that the AMBz is highly efficient for the corrosion inhibitor for the carbon steel in 2.0 M phosphoric acid and 1.0 M HCl chloridric acid. IE was found to be increased with increasing inhibitor concentration but decrease with increasing temperature. The IE%

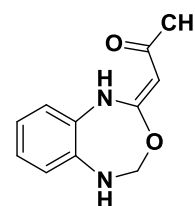


Fig. 14. 4-Acetylmethylene-1,5-benzodiazepine-2-one (AMBz).

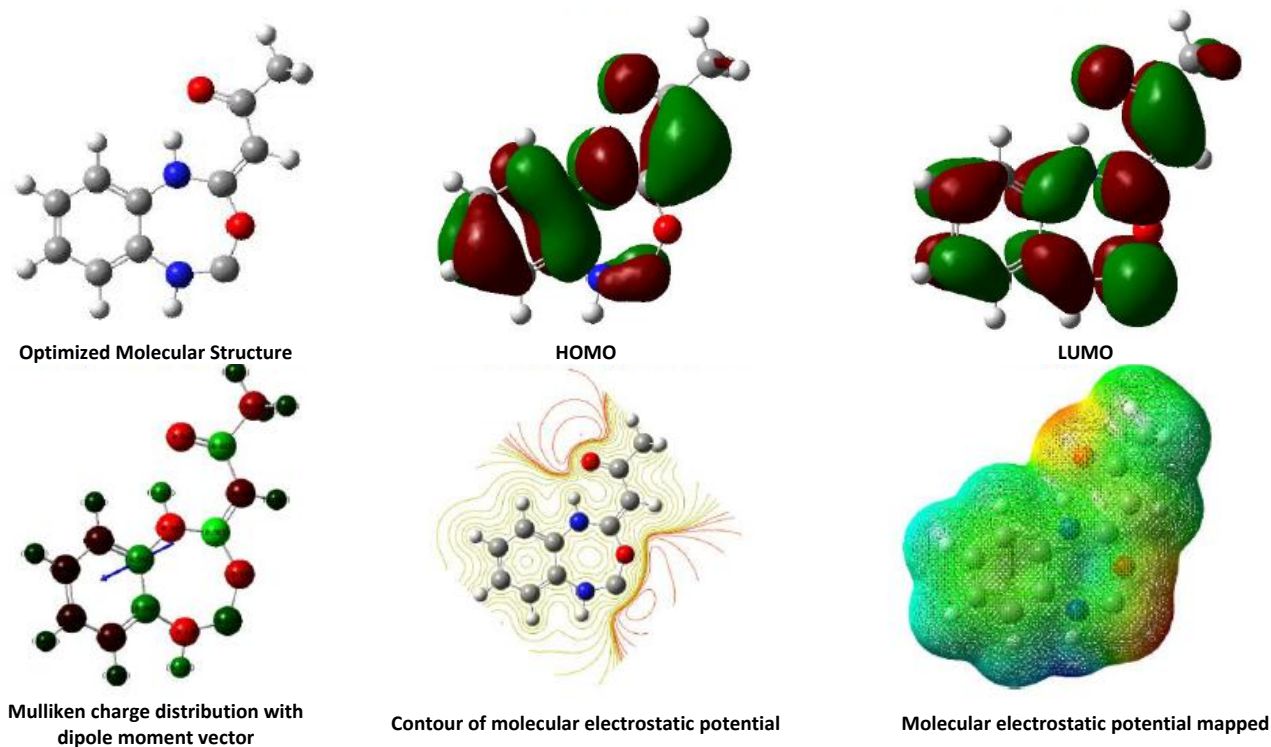


Fig. 15. Optimized structure, frontier molecular orbital density distributions, Mulliken charges with dipole moment and electrostatic properties of AMBz.^[91]

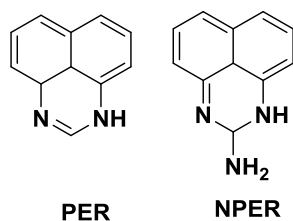


Fig. 16. Molecular structures of 1H-perimidine (PER) and 1H-perimidin-2-amine (NPER).

reaches 90% and 85% in HCl and phosphoric acid mediums, respectively. Polarization studies showed that this compound was cathodic inhibitor. The inhibition action of this compound obey Langmuir adsorption isotherm. The experimental results are further verified with quantum chemical parameters calculated at DFT/B3LYB/6-31G (d, p) and the Monte Carlo simulation results. Figures 14 and 15 show the optimized structure, frontier molecular orbital density distributions, Mulliken charges with dipole moment and electrostatic properties of AMBz. The authors have discussed the quantum chemical parameters (such as EHOMO, ELUMO, and dipolar moment) for AMBz. The EHOMO and ELUMO values of AMBz are

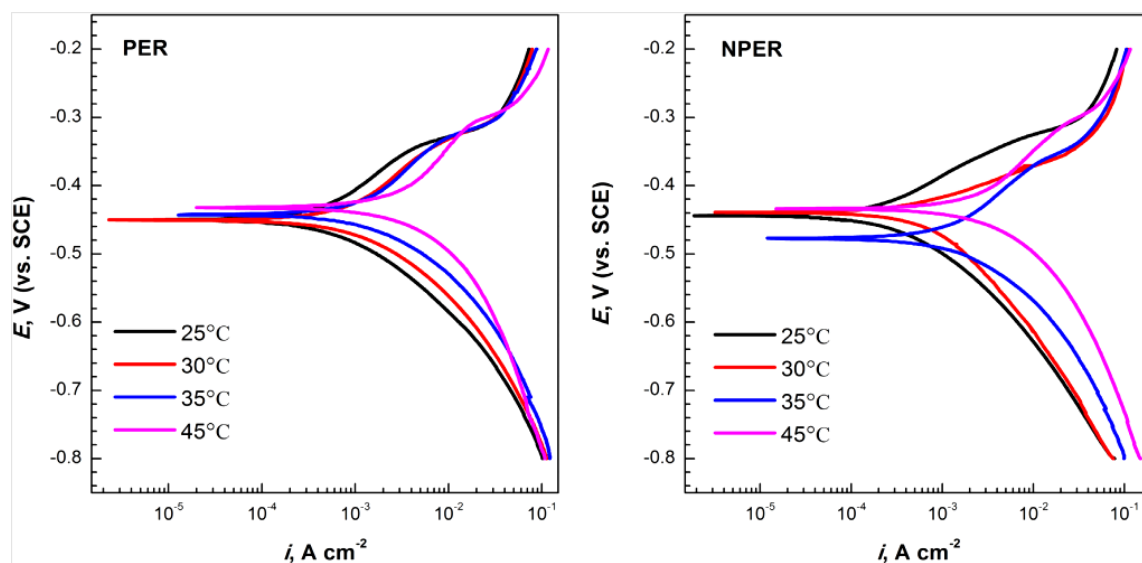
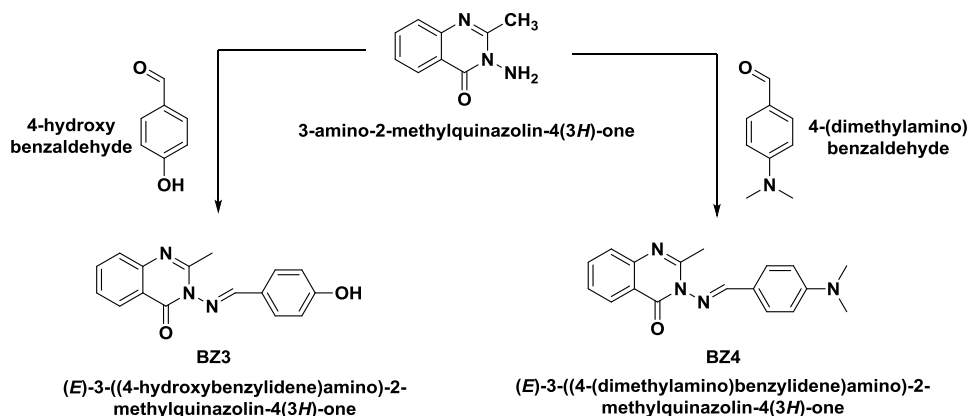
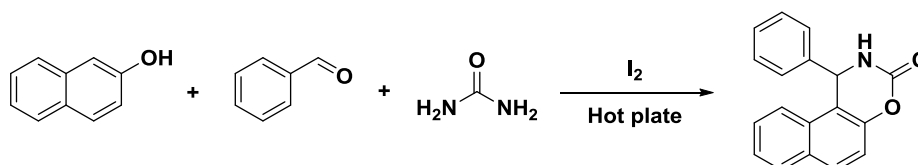
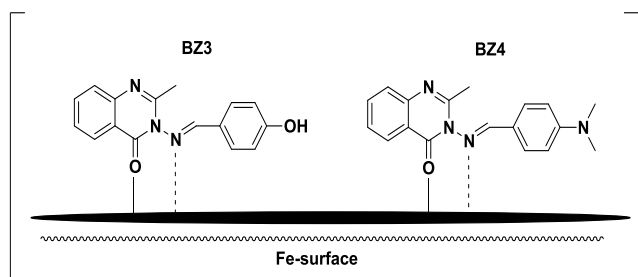


Fig. 17. Tafel curves for mild steel in 1.0 M HCl solution in the presence of 0.06 mM PER and NPER at different temperatures.^[92]

Scheme 6. Preparation of corrosion inhibitors, BZ3 and BZ4.^[93]Scheme 7. Synthetic scheme and molecular structure of the 1-phenyl-1,2-dihydronaphtho[1,2-e]-[1,3]oxazin-3-one (PNO).^[94]Fig. 18. Proposed inhibition mechanism of BZ3 and BZ4.^[93]

found to be -5.7870 and -1.7733. The results clearly show that the heteroatoms and π -system of AMBz play a crucial role in the IE values.

He et al.,^[92] investigated 1H-perimidine (PER) and 1H-perimidin-2-amine (NPER) (Fig. 16) as corrosion inhibitors for mild steel in acidic media. The inhibition ability of the PER and NPER are confirmed by means of EIS, potentiodynamic polarization and theoretical calculations. These compounds showed over 90% IE at a concentration of 0.15 mM. However, the IE is slightly higher for NPER when compare to PER due the presence of additional amino-group at the 2-position. The results suggest that the fusion of large π -bond system with N-containing heterocycles makes the compounds strongly adsorb on iron surfaces in a nearly parallel mode. The adsorption of PER and NPER molecules obeys Langmuir isotherm temperatures. The results show that the both anodic and cathodic reactions of corrosion process are simultaneously impeded in the presence of inhibitors and suggesting mixed mode of inhibition of the PER and NPER.

Jamil et al.,^[93] prepared corrosion inhibitors, 3-((4-hydroxybenzylidene)amino)-2-methylquinazolin-4(3H)-one (BZ3) and

3-((4-(dimethylamino)benzylidene)amino)-2-methylquinazolin-4(3H)-one (BZ4), and the structure of the compounds are characterized by spectroscopic techniques (Scheme 6). They found that the inhibitors BZ3 and BZ4 are excellent inhibitors against mild steel corrosion in 1 M HCl solution. The BZ3 and BZ4 achieved maximum inhibition efficiency of 96 and 92% respectively. Results depicts that the inhibition efficiency increased with increasing inhibitor concentration, whereas it decreased with increasing temperature. Microscopic results confirmed the formation of protective film on the mild steel surface by BZ3 and BZ4 molecules. Quantum chemical calculations are also performed to elucidate the relationship between the electronic structures of the BZ3 and BZ4 molecules and IE. Results revealed that a substituent in the meta position on the inhibitor structure decreased the IE, whereas a substituent in the para position enhanced the IE. Fig 18 showed inhibition mechanism of BZ3 and BZ4 towards mild steel inhibition in 1 M HCl.

Singh et al.,^[94] reported naphthoxazinone derivative 1-phenyl-1,2-dihydronaphtho[1,2-e]-[1,3]oxazin-3-one (PNO) as corrosion inhibitor for J55 steel in 3.5 wt% NaCl solution saturated with CO₂. The PNO was prepared by stirring a mixture of β -naphthol, benzaldehyde, urea and I₂ hot plate at 80°C for 5 min (Scheme 7). Corrosion inhibition efficiency was calculated by using weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. The formation of productive layer by 1-phenyl-1,2-dihydronaphtho[1,2-e]-[1,3]oxazin-3-one (PNO) was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The results indicated that the naphthoxazinone derivative molecule behaved as a mixed type inhibitor. The mixed type inhibitors reduce both the anodic and the cathodic electrochemical reactions. They found that the inhibition efficiency of PNO increased with a concentration (90.4% at 500 mg L⁻¹). The adsorption of

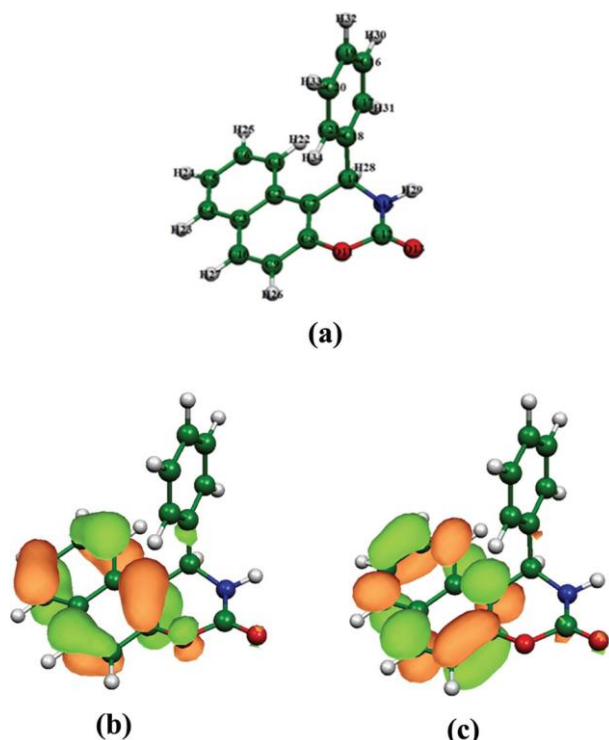


Fig. 19. (a) Optimized geometry of the inhibitor; (b) HOMO and (c) LUMO frontier molecular orbitals of the 1-phenyl-1,2-dihydronaphtho[1,2-e]-[1,3]oxazin-3-one (PNO).^[94]

naphthoxazinone derivative on mild steel obeyed the Langmuir isotherm. Thermodynamic values indicated spontaneous adsorption of naphthoxazinone derivative on the surface of mild steel involving both physical and chemical interaction. The quantum chemical calculations and molecular dynamics revealed a planar of PNO with strong affinity towards the mild steel surface. Fig. 19 shows the HOMO and LUMO frontier molecular orbitals of the 1-phenyl-1,2-dihydronaphtho[1,2-e]-[1,3]oxazin-3-one (PNO). The results conclude that the geometrical structure of inhibitor molecule is ideal. In general, to achieve strong adsorption on a flat surface, the inhibitor molecules must possess a planar structure. The values of bond angles confirm the planar orientation of the PNO. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses are very useful techniques to study the formation of productive layers on the surface of steel by inhibitor molecules. Fig. 20 shows the SEM

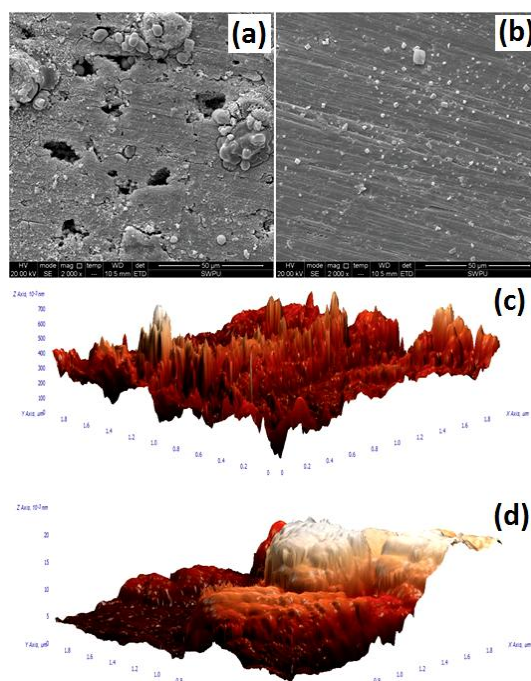
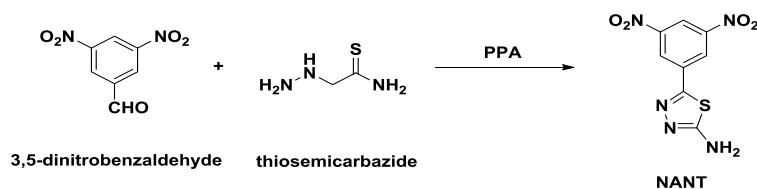


Fig. 20. SEM and AFM images (a, c) in the absence of inhibitor and (b, d) in the presence of 1-phenyl-1,2-dihydronaphtho[1,2-e]-[1,3]oxazin-3-one (PNO).^[94]

and AFM images of J55 steel surface with and without optimum concentration of PNO. The J55 steel surface with inhibitor showed smooth surface, whereas, the surface became very rough when it exposes to the 3.5 wt% NaCl solution saturated with CO₂.

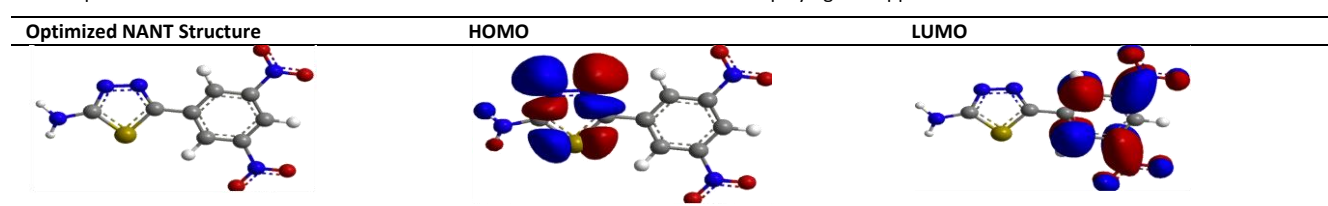
7. Heterocyclic Compounds Containing N, O, and S

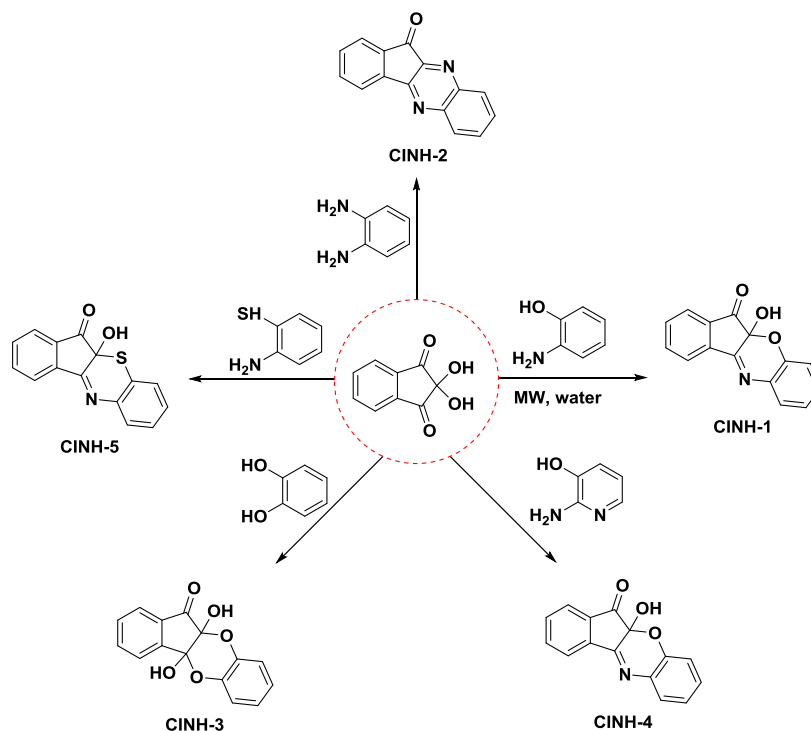
Al-Baghdadi et al.,^[95] prepared new heterocyclic compound, 3-nitro-5-(2-amino-1,3,4-thiadiazolyl)nitrobenzene (NANT), and used as efficient corrosion inhibitor for the mild steel in 1 M HCl. Scheme 8 shows the synthesis of NANT. They found that the NANT is mixed-type inhibitors with predominantly cathodic inhibitive effects. The NANT found to have good activity towards the corrosion inhibition of mild steel (1 M HCl) and microbial corrosion. The activity increased with the concentration of NANT. The NANT inhibited the mild steel



Scheme 8. Synthesis of NANT.^[95]

Table 3 Optimized structure and the HOMO and LUMO orbitals for NANT molecule in employing DFT approach.





Scheme 9. Microwave-induced aqueous phase synthesis of five novel environmental friendly heterocyclics (CINH-1, CINH-2, CINH-3, CINH-4, and CINH-5).

by forming protective film *via* physical adsorption on the steel surface. The adsorption obeyed Langmuir isotherm. The N-atom of the carbazole ring and pi-electron centres of NANT is the main reason for the inhibitive action (Table 3).

Mishra and co-workers^[96] reported microwave-induced aqueous phase synthesis of five novel environmental friendly heterocyclics (CINH-1, CINH-2, CINH-3, CINH-4, and CINH-5) containing N, O, and S (Scheme 9). The heterocyclics showed excellent inhibitive action towards corrosion of mild steel in 1 M HCl. At 39.8×10^{-5} M concentration, the CINH-1, CINH-2, CINH-3, CINH-4, and CINH-5 gave 82.38, 85.79, 88.93, 92.61, and 95.45% of inhibition. Results showed that inhibitors are cathodic-type and the adsorption of CINH molecules at the interfaces obeys Temkin adsorption isotherm.

Ahmed et al.,^[97] prepared by six heterocyclic compounds such as 4-(4-amino-5-mercapto-4H-1,2,4-triazole-3-yl) phenol (ATT1), 4-amino-5-(4-aminophenyl)-4H-1,2,4-triazole-3-thiol (ATT2), 4-amino-5-(4-((4-nitrobenzylidene)amino)phenyl)-4H-1,2,4-triazole-3-thiol (ATT4), 4-amino-5-(4-((4-chlorobenzylidene)amino)phenyl)-4H-1,2,4-triazole-3-thiol (ATT5), 4-amino-5-(3,4-diaminophenyl)-4H-1,2,4-triazole-3-thiole (ATT6) and 4-((4-nitrobenzylidene)amino)-5-(4-(((Z)-4-nitrobenzylidene)amino)phenyl)-4H-1,2,4-triazole-3-thiol(ATT3) (Fig. 21). The inhibition ability of ATT 1, ATT 2, ATT 3, ATT 4, ATT 5 and ATT 6 was studied for the corrosion of mild steel in 0.5 M HCl. The order of inhibition efficiency was ATT 5 > ATT 1 > ATT 2 > ATT 3 > ATT 6 > ATT 4. Maximum inhibition efficiency of 95% was achieved by ATT 5. The formation of inhibitor layer on the steel surface inhibits the corrosion of the mild steel. The adsorption process of ATT molecules follows Langmuir adsorption isotherm.

New 3,5,12-trithia-1,7,14-triaza-tricycle [5.3.3.27,10] tetradeca-6(14), 9-dien-8-one was prepared and the structure was confirmed by various spectral techniques (Scheme 10).^[98] The prepared

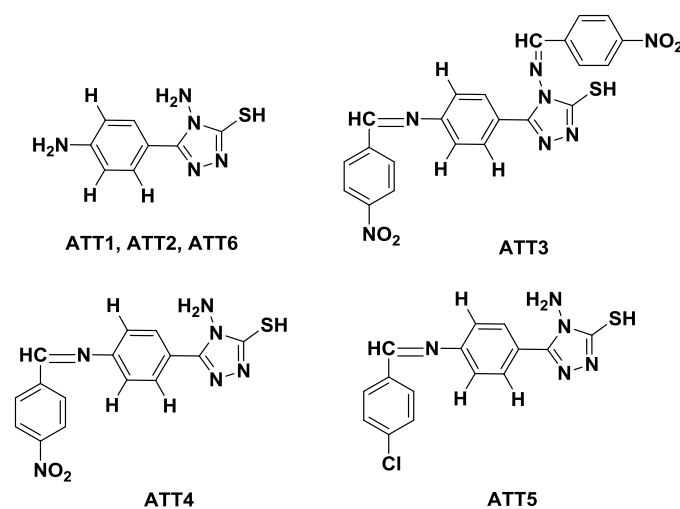
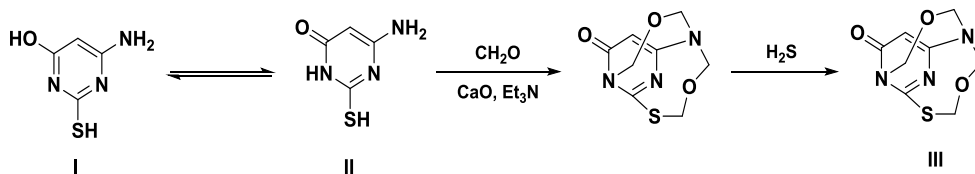


Fig. 21. Structure of ATT 1, ATT 2, ATT 3, ATT 4, ATT 5 and ATT 6.^[97]

compounds was used as corrosion inhibitor for corrosion crude oil pipelines (N-80 type) in saline water as a corrosive medium and the inhibition efficiency was calculated by means of weight loss method and electrochemical techniques such as potentiodynamic polarization and EIS. SEM-EDX was used to investigate the productive layer formation on N-80 type steel surface by inhibitor molecules. Maximum inhibition values of 90.12%, 90.62%, 79.70% and 90.05% were calculated by weight loss method, polarization technique, EIS and EDS, respectively (Fig. 22). The excellent corrosion inhibition performance is mainly due to the presence of heteroatom (N, O and S) in the inhibitor.



Scheme 10. Shows the one pot reaction of heterocyclic compound.^[98]

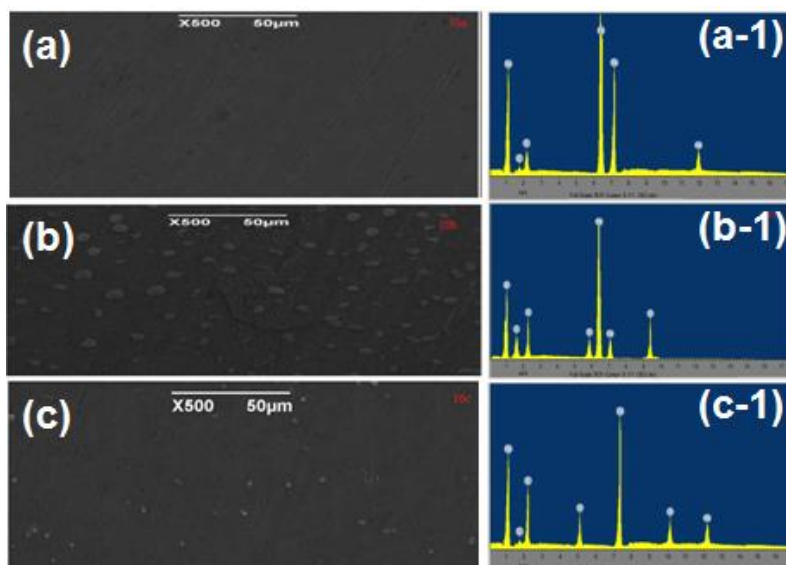


Fig. 22. SEM images and corresponding EDS spectra of carbon steel surface (a, a-1) carbon steel (reference), (b, b-1) carbon steel surface in absence of inhibitor and (c, c-1) carbon steel surface with presence of inhibitor.^[98]

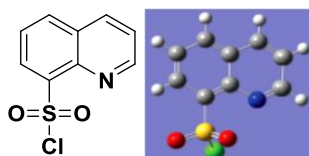


Fig. 23. Molecular and optimized structure of 8-quinoline sulphonyl chloride (8-QSC).^[99]

Meften et al.,^[98] used SEM-EDS analysis proved the corrosion inhibition property of inhibitor, 3,5,12-trithia-1,7,14-triaza-tricycle [5.3.3.27,10] tetradeca-6(14), 9-dien-8-one. They found that the polished N-80 type steel is smooth with the elemental content of 98.227% Fe and 0.20% of C (0% of corroded Fe), whereas after exposure to the corrosive environment, the surface found to be very rough with pits and cracks. The elemental content of N-80 type steel (after exposure to the corrosive environment) was found to be 66.91% Fe (remaining), 31.88% Fe (corroded), 11.81% C and 22.54% O. Surprisingly, the N-80 type steel with inhibitor showed smooth surface and the weight percentage of corroded Fe was found to be 3.17%. The results confirmed the excellent corrosion inhibition property of 3,5,12-trithia-1,7,14-triaza-tricycle [5.3.3.27,10] tetradeca-6 (14), 9-dien-8-one.

Sundaram et al.,^[99] studied corrosion inhibition activity of 8-quinoline sulphonyl chloride (8-QSC) on mild steel in 1 M HCl solution. Fig. 23 shows molecular and optimized structure of 8-quinoline sulphonyl chloride (8-QSC). Weight loss (WL) method and electrochemical measurements, namely, EIS, Tafel polarization (TP), and linear polarization resistance (LPR) were performed to evaluate the corrosion inhibition activity of 8-QSC for mild steel in 1M HCl solution. Results confirmed that the 8-QSC is a good corrosion

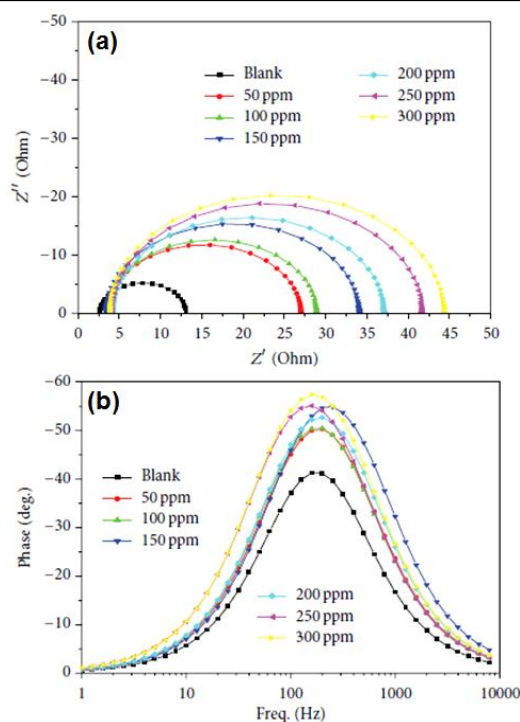


Fig. 24. (a) Electrochemical impedance (Nyquist) spectrum of mild steel in 1M HCl solution with and without various concentrations of inhibitor. (b) Electrochemical impedance (Bode) spectrum of mild steel in 1M HCl solution with and without various concentrations of inhibitor.^[99]

inhibitor for mild steel in 1 M HCl solution. Fig. 24 shows the electrochemical impedance (Nyquist and Bode) spectrum and potentiodynamic polarization curves of mild steel in 1M HCl solution with and without various concentrations of inhibitor. The following points are concluded from the results;

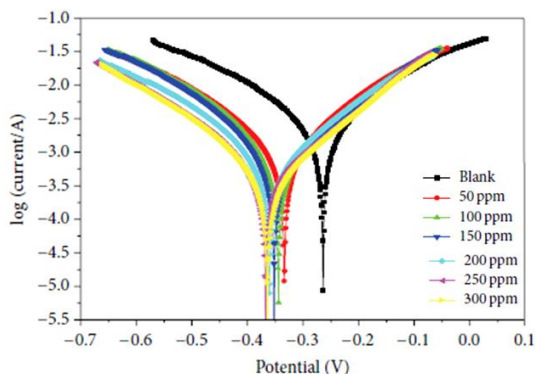


Fig. 25. Potentiodynamic polarization curves of mild steel in 1M HCl solution with and without various concentrations of inhibitor.^[99]

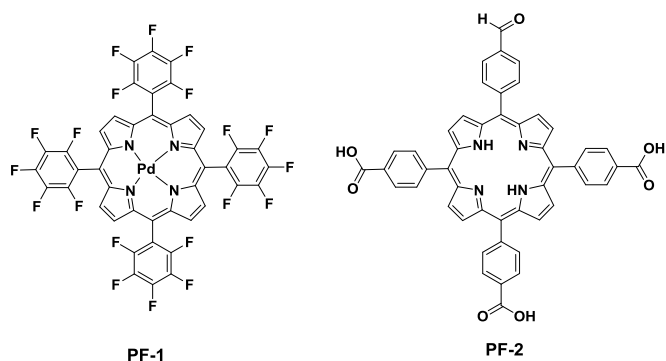


Fig. 26. Structure of porphyrins, 5,10,15,20-tetrakis(pentafluorophenyl)-21H,23Hporphyrin palladium(II) (PF-1) and 4,4',4'',4'''-(porphyrin-5,10,15,20-tetrayl)tetrakis(benzoic acid) (PF-2).^[100]

- ✓ IE increased with increase in inhibitor concentration
- ✓ Inhibitor molecules form protective film on the surface of mild steel
- ✓ Adsorption of 8-QSC on the mild steel surface follows Langmuir adsorption isotherm
- ✓ Tafel plot indicates that the used inhibitor behaves predominantly as cathodic type
- ✓ The values of ΔG_0 proved the strong physisorption of 8 QSC molecules on mild steel surface

Nyquist plots in Fig. 25 shows that the diameter of the semicircle increases with inhibitor concentration, indicating the inhibition processes are charge transfer controlled. Alike, the continuous increase in the phase angle shift with the inhibitor concentration confirms the formation adsorptive film by inhibitor molecules. Tafel plots are used to confirm the type of inhibitor, whether the inhibitors or mixed type, cathodic or anodic. If the change in E_{corr} is greater than 85 mV with respect to blank, the inhibitor can be classified as cathodic or anodic type. In the case of 8-QSC inhibition, the shift is over 85 mV, therefore, the 8-QSC classified as cathodic inhibitor.

8. Heterocyclic Porphyrin Compounds

Singh and co-workers^[100] reported two heterocyclic porphyrin compounds, namely, 5,10,15,20-tetrakis(pentafluorophenyl)-21H,23Hporphyrin palladium(II) (PF-1) and 4,4',4'',4'''-(porphyrin-5,10,15,20-tetrayl)tetrakis(benzoic acid) (PF-2) (Fig. 26), as corrosion

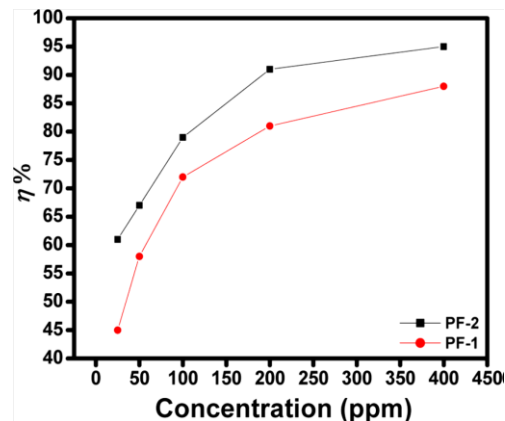


Fig. 27. Plot of the inhibitor concentration vs inhibition efficiency.^[100]

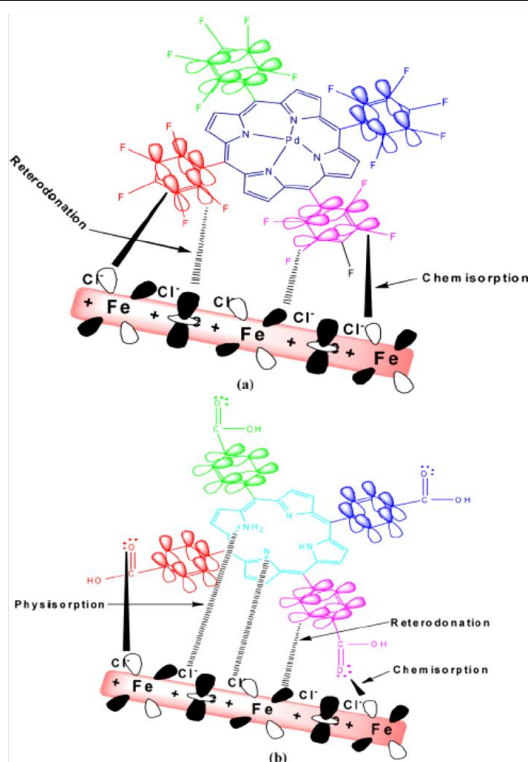


Fig. 28. Mechanism of corrosion mitigation of J55 steel in the presence of (a) PF-1, (b) PF-2, and inhibitor in 3.5% NaCl solution saturated with CO_2 .^[100]

for J55 steel in a sweet corrosion environment (3.5 wt % NaCl + CO_2). Various measurements such as weight loss and electrochemical methods were used to test the inhibitors. Thermodynamics studies confirmed that the adsorption of PF-1 and PF-2 molecules on the J55 steel follows Langmuir adsorption isotherm. The inhibition efficiency of the PF-1 and PF-2 increased with concentration. Fig. 27 depicts that the inhibition efficiency of PF-2 (93%) is more than that of PF-1 (85%). The mechanism of corrosion mitigation of J55 steel in 3.5% NaCl solution saturated with CO_2 with the presence of PF-1 and PF-2. The N, F, and O present in the PF-1 and PF-2 molecules assists to form bonds/complexes with the J55 steel and protects from the attack of 3.5% NaCl solution saturated with CO_2 . In addition, the unshared π -electrons (conjugated bonds and aromatic rings) also contribute in the complex formation between the J55 steel and the inhibitor. The lone pair of electrons is donated to the vacant d-

orbitals of the Fe atoms (chemical adsorption) and filled orbitals of Fe gives back electrons to inhibitor molecules via reterodonation (back-bonding) thus, forming a strong protection layer (Fig 28).

Recently, three triazine derivatives namely 4-((2-(5,6-diphenyl-1,2,4-triazin-3-yl)hydrazineylidene)methyl)-N,N-dimethylaniline (HT-1), 3-(2-(4-methoxybenzylidene) hydrazineyl)-5,6-diphenyl-1,2,4-triazine (HT-2), 2-(2-(5,6-diphenyl-1,2,4-triazin-3-yl)hydrazineylidene)methyl)phenol (HT-3), ceftriaxone, [[4-Hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-phenyl-methyl]-urea (HPU1) and [[4-Hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-(4-methoxy-phenyl)-methyl]-urea (HPU2) are also used as corrosion inhibitors for mild steel in 1 M HCl solution.^[101, 102]

Overall, the heterocyclic compounds are the most efficient candidates for the corrosion inhibition of Fe-steel in acidic medium.

4. Conclusions

Heterocyclic compounds are effectively used as corrosion inhibitor for steel under various aggressive environments. Based on the chemical structure, electrostatic forces, steric factors, aromaticity, electron density, p-orbital character, electronic structure and availability, heterocyclic are proven to be the efficient inhibitors for corrosion of metals. The heterocyclic compounds inhibit the steel surface by forming protective film on the steel surface. The inhibition of heterocyclic compounds maybe anodic or cathodic or mixed type. Most of the inhibitors showed increasing trend in the inhibition efficiency with concentration of inhibitor. Overall, this review has summarized the heterocyclic compounds that are used for the corrosion inhibition of steels in various aggressive environments. In addition, heterocyclic compounds reported for the corrosion inhibition of steel in CO₂ saturated brine environment are also highlighted. Detail mechanisms involved in the inhibition processes are also discussed.

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Conflicts of Interest

Authors declare no conflict of interest.

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