



## Corrosion inhibition of thiourea and thiadiazole derivatives : A Review

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### Abstract

The continuous search for better corrosion inhibitors, due to vast differences in the media encountered in industry remains a focal point in corrosion control. The use of organic compounds to inhibit corrosion has assumed great significance due to their application in preventing corrosion under various corrosive environments. These compounds have great potential to inhibit aqueous corrosion due to film formation by adsorption on the metal surface. This paper reviews the inhibitive effect of thiourea and thiadiazole derivatives. This group of organosulphur and heterocyclic compounds and derivatives has important theoretical and practical applications, but their inhibition mechanism is not fully understood, despite extensive study. The effect of these compounds on the corrosion of metallic alloys was evaluated through assessment of various journals and experimental techniques. The corrosion rate was found to be a function of different variables. Due attention was paid to the systematic study of inhibitor action of derivatives with much emphasis on the functional groups of the molecular structure. From the comprehensive discourse presented, it is concluded that the derivatives fulfill the basic requirements for consideration as an efficient corrosion inhibitor.

### Introduction

Corrosion is an electrochemical process by which metallic structures are destroyed gradually through anodic dissolution [1]. This phenomenon necessitates the continuous search for better corrosion inhibitors, due to vast differences in the media encountered in industry which remains a focal point in corrosion control as inhibitors slowdown the corrosion process on metals. Corrosion is one of the main concerns in the durability of materials and structures; as a result, studies are continually carried out to develop an effective means of corrosion control. Selection of an appropriate inhibitor for a particular system is actually complicated, due to their specificity and great variety of corrosion-related applications. The corrosion of stainless steel in acidic solutions is a fundamental academic and industrial concern that has received a considerable amount of attention [1]. Stainless steel is covered with a highly protective film of chromium oxyhydroxide and is resistant to corrosion in many aggressive environments; however, acidic solutions are aggressive to this film layer and results in severe pitting formation [2, 3, 4]. Several mineral acid solutions are widely used for various treatments of materials in industry such as pickling, descaling, acid cleaning and oil-well acidizing, thus the presence of corrosion inhibitors is very important to keep the surface of steel intact and reduce their corrosion rates [5, 6]. The highly corrosive nature of aqueous mineral acids on most metals requires degree of restraint to achieve economic maintenance, operation of equipment, minimum loss of chemical product and maximum safety condition.

Corrosion inhibitors adhere to the metal/metal oxide surface [e.g., through chemisorption, physisorption, complexation, or precipitation] and prevent the access of oxygen to the cathode. This prevents the diffusion of hydrogen from the cathode, or inhibit [anodic inhibitors] the dissolution of the metal. The inhibition efficiency [IE] depends on the parameters of the corrosive system [pH, temperature, duration, metal composition, etc.] and on the

structure of the inhibitor molecule. Inhibitors reduce, or prevent reaction between a metal and its surroundings when added to the medium in small quantities. The use of inhibitors is one of the most practical methods for protection against corrosion, especially in the extraction and processing of petroleum, gas and in other chemical and petrochemical industries, heavy industrial manufacturing, water treatment facility, water-containing hydraulic fluids, engine coolants, ferrous metal cleaners, automatic transmission fluids, automotive component manufacture, cutting fluids etc [7].

Despite the great number of studies devoted to the subject of corrosion inhibitors most of what is known is as a result of trial and error, both in the laboratory and the fields. Historically, the development of corrosion inhibitors has always been determined by their effectiveness, and they were often based on ecologically problematic heavy metal. The development of new corrosion inhibitors of non-toxic type, which do not contain heavy metals and inorganic phosphates, is of considerable importance [4]. Inorganic compounds such as chromate, dichromate, nitrite and nitrate are widely used as corrosion inhibitors in several media and for different metals and alloys, on the other hand, the biotoxicity of these products, especially chromate, is well documented as well as their non-environmental-friendly characteristics which limit their application[5,6]. Among alternative corrosion inhibitors, organic products containing one or more polar functions have proven to be quite efficient in minimizing the effect of corrosion in addition to heterocyclic compounds containing polar groups and  $\pi$ -electrons [8, 9]. Effective inhibitors are expected to perform under a wide range of conditions; hence, special attention must be paid to the selection of inhibitors for such practical applications [10].

## **ORGANIC INHIBITORS**

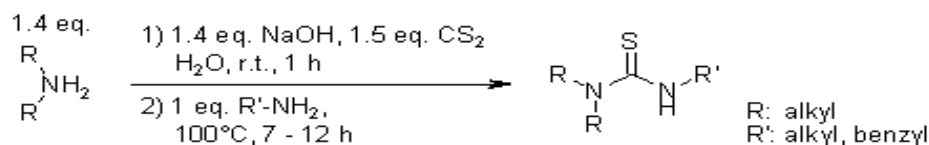
The use of organic compounds to inhibit corrosion has assumed great significance due to their application in preventing corrosion under various corrosive environments [11]. These compounds have shown great effectiveness for inhibiting aqueous corrosion due to film formation on the metal surface [12, 13]. The inhibiting action of organic compounds is attributed to interactions with metallic surfaces by adsorption. The polar function is frequently regarded as the reaction center for the adsorption process establishment [14], being the adsorption bond strength determined by the electron density and polarisability of the functional group. The molecular structure of organic compounds exerts a major influence on the extent of inhibition, thus the effect of the functional atom in the adsorption processes varies because of the very different situation created by changing various factors such as medium and inhibitor in the system [15, 16, 17]. The adsorption provides information about the adsorbed molecules themselves as well as their interaction with the metal surface [18]. Organic inhibitors displaces water molecules from the metal surface, and then interact with anodic and/or cathodic corrosion reaction and prevent transportation of water and corrosive-active species to the surface, thus preventing cathodic and anodic reactions or both together. The effect is obtained through the formation of a diffusion barrier or by blocking reaction sites. Most organic inhibitors are adsorbed on the metal by surface water molecule displacement, forming a compact barrier [19]. A variety of organic compounds have been reported to be effective as corrosion inhibitors during acidization in industrial cleaning processes [11]. Studies report that the adsorption of the organic inhibitors mainly depends on some physicochemical properties of the molecule to the possible steric effects and electronic density of donor atoms; adsorption is suppose also to depend on the possible interaction of p-orbitals of the inhibitor with d-orbitals of the surface atoms, which induce greater adsorption of the inhibitor molecules onto the surface of the metal alloy, leading to the formation of a corrosion protecting film [20]. Ormellese et al researched about 80 organic substances such as: primary and tertiary amines and alkanolamines, amino acids, mono and poly-carboxylates. Such substances are selected with the purpose of analysing the effect of functional groups [aminio or carboxylic], the position and number of the substituent and to study the influence of either electron-donor [nucleophile groups like oxidrilic, aminic and alkyl groups] or electron-attractor groups [electrophile agents like halogen, carboxylic group and atoms with high electronegativity], as well as the effect of carbon-chain length [21]. Unfortunately, most of the organic inhibitors used are very expensive and harzadous. Their toxic properties limit the extent of application. Thus, it remains an important objective to find low-cost inhibitors of the non-hazardous type for the protection of metals against corrosion.

## THIOUREA

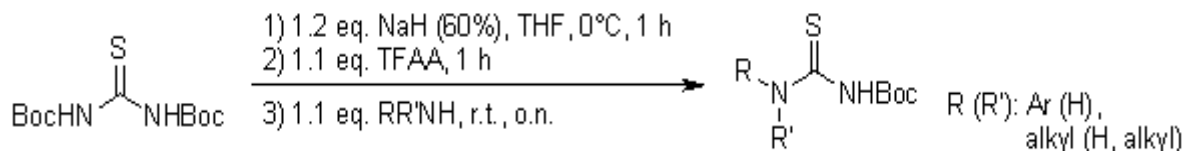
Thiourea is an organosulfur compound with the formula  $\text{SC}[\text{NH}_2]_2$ . It is structurally similar to urea, except that the oxygen atom is replaced by a sulfur atom, but the properties of urea and thiourea differ significantly. Thiourea is a reagent in organic synthesis. "Thioureas" refers to a broad class of compounds with the general structure  $[\text{R}^1\text{R}^2\text{N}][\text{R}^3\text{R}^4\text{N}]\text{C}=\text{S}$ . Thioureas are related to thioamides e.g.  $\text{RC}[\text{S}]\text{NR}_2$ , where R is methyl, ethyl, etc.

### Synthesis of thiourea

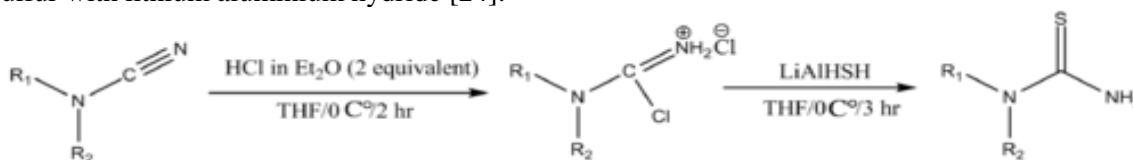
A simple condensation between amines and carbon disulfide in aqueous medium allows an efficient synthesis of symmetrical and unsymmetrical substituted thiourea derivatives. This protocol works smoothly with aliphatic primary amines to afford various di- and tri-substituted thiourea derivatives [22].



Stable and readily available *N,N'*-di-Boc-substituted thiourea can be used as a mild thioacylating agent when activated with trifluoroacetic acid anhydride. Through thioacylation of nucleophiles, such as amines, alcohols, thiols, sodium benzenethiolate, and sodium malonates, a series of thiocarbonyl compounds were prepared with good chemical selectivity and functional group tolerance [23].



*N,N*-unsubstituted thioureas are generally prepared by allowing the corresponding cyanamide to react with  $\text{LiAlHSH}$  in the presence of 1 N HCl in anhydrous diethyl ether.  $\text{LiAlHSH}$  can be prepared by reacting sulfur with lithium aluminium hydride [24].



Thiourea reduces peroxides to the corresponding diols. The intermediate of the reaction is an unstable epidioxide which can only be identified at . Epidioxide is similar to epoxide except with two oxygen atoms. This intermediate reduces to diol by thiourea.

### MECHANISM OF INHIBITION OF THIOUREA

As the thiourea molecule contains one sulphur and two nitrogen atoms, thiourea and its derivatives are potential corrosion inhibitors [25]. The availability of lone pair electrons in the inhibitor molecules facilitates the electron transfer from the inhibitor to the metal, forming a coordinate covalent bond [26]. The corrosion inhibitor acts as a protective film of which the strength of the adsorption bond depends on the electron density, the donor atom of the functional group and also on the polarisability of the group. The organic substances belonging to this group contain mainly oxygen, sulfur, nitrogen atoms, and multiple bonds in the molecules that facilitate the adsorption on the metal surface [27].

The corrosion inhibition of thiourea is superior to amine-based inhibitors in acidic media; this inhibitor simultaneously acts in both anodic and cathodic areas. The multiple bonds in the molecules facilitate adsorption on the metal surface and are strongly polar [28]. According to refs. [29] and [30], sulfur compounds, such as thiourea, are very effective inhibitors for steel in acidic conditions because sulfur atom is easily protonated in acidic solution and a stronger electron donor than nitrogen. Therefore sulfur atom is more strongly adsorbed to the metal surface. It has been observed that adsorption mainly depends on the presence of  $\pi$ -electrons and heteroatoms, which induce greater adsorption of the inhibitor molecules onto the surface of metal. All thiourea derivatives suppress  $H_2$  pickup by blocking the active sites on the steel surface [31]. Kuznetsov [32] studied the mechanism of action of inhibitors and considered that most chemical reactions can be treated as acid–base interactions. Based on this concept, thiourea would act as a rather strong base due to its sulphur, which serves as an electron donor. On the other hand on iron [ $Fe^{3+}$ ,  $Fe^{2+}$  and metallic iron] thiourea would behave like acids. Herein, they act as electron acceptors, with higher acidity corresponding to higher oxidation state. This interaction with the inhibitor would proceed mainly due to the presence of long-range electrostatic forces [32]. The study of corrosion of iron is a matter of tremendous theoretical and practical concern and has received a considerable amount of interest. Corrosion inhibition of iron by organic inhibitors in aqueous media, especially in acidic media, has also been studied extensively in considerable detail.

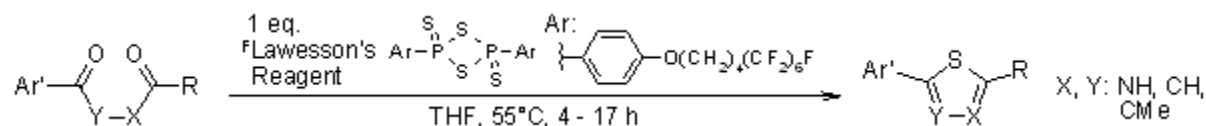
It has been reported that sulphur-containing inhibitors are useful in sulphuric acid solution, while N-containing inhibitors exert their best efficiencies in hydrochloric acid [33]. Thiourea has high inhibition efficiency at low concentration and loses its efficiency at high concentrations. The acceleration of corrosion at a higher concentration of thiourea is explained in several different papers [34-38], but no satisfactory explanation is given. The inhibition efficiency of thiourea and its N-substituted derivatives is controlled by the adsorption of molecular species, which increases the inhibition, and the protonated species, accelerating the rate of corrosion. The protonation process is controlled by the charge density on the sulphur atom, lengthening and weakening of the C–S bond and the reactivity of the molecule. The effect of protonation increases with increasing concentration of thiourea. Substitution of the H-atom of the  $-NH_2$  group in the parent compound thiourea affects the metal–sulphur interaction and protonation. The steric and electronic factors of the substituents change the adsorption characteristics affecting inhibition performance [39].

## THIADIAZOLE

Thiadiazole is any of several isomeric five membered heterocycles having two carbon atoms, two nitrogen atoms, one sulphur atom and two double bonds.

### Synthesis of Thiadiazole

Thionation of amides, 1,4-diketones, *N*-[2-oxoalkyl]amides, and *N,N'*-acylhydrazines with the use of a fluororous Lawesson's reagent leads to thioamides, thiophenes, 1,3-thiazoles, and 1,3,4-thiadiazoles in high yields. The isolation of the final products is achieved in most cases by a simple filtration [40].



### MECHANISM OF INHIBITION OF THIADIAZOLE

The inhibition property of thiadiazole compounds is attributed to their molecular structure. The planarity and pairs of free electrons in heteroatoms are important characteristics that determine the adsorption of these molecules on the metal surface. Thiadiazole derivatives are considered as non-cytotoxic substances. This environmentally friendly property makes them favorable to be used in practice, replacing some toxic organic inhibitors in agreement with the new environmental restrictions need to use green ones. [41, 42].

Various thiadiazole compounds have been evaluated as corrosion inhibitors for mild steel in acidic chloride and sulphate solutions [43-49]. The inhibition efficiency is generally affected by the chemical changes occurring to the inhibitor, by the nature and surface charge of metal and by the type of the aggressive electrolytic medium, and is ascribed to the effect of functional groups connected with aromatic rings. The primary step in the mechanism of inhibition by these organic compounds is generally accepted as the adsorption of the inhibiting species on the metal surface [50, 51]. The polar function is frequently regarded as the reaction centre for the adsorption process establishment, and the adsorption bond strength is determined by the electron density and polarisability of the functional group [52].

Inhibitors influence the kinetics of the electrochemical reactions which constitute the corrosion process and thereby modify the metal dissolution in acids. The adsorption itself depends to a great extent on the molecular structure. To this problem of dissolution is dedicated a number of investigations [53-56]. The adsorption of inhibitors takes place through heteroatom such as nitrogen, oxygen, phosphorus and sulphur, triple bonds or aromatic rings. Generally, the tendency to form a stronger coordination bond and, as consequence, inhibition efficiency should increase in the order of  $O < N < S < P$ . The molecules that, at the same time, contain nitrogen and sulphur in their structures are of particular importance, since these provide an excellent inhibition compared with the compounds that contain only sulphur or nitrogen [57].

Thiadiazole inhibitors are believed to be adsorbable, not only on the cathodic sites by electrostatic attraction using the charge of the protonated molecule, but also on the anodic sites by virtue of donation of the electron-pair on the nitrogen atom of the unprotonated molecule [58]. The presence of thiadiazole derivatives in acidic solution inhibits both the hydrogen evolution and the anodic dissolution processes. This could be interpreted as an action of mixed inhibitor control over the electrochemical semi-reactions. The adsorption of the thiadiazole on the metal surface occurs either directly, on the basis of donor acceptor interactions between the p-electrons of the hetero atoms and the vacant d-orbital of iron surface atoms, or interaction of thiadiazole derivatives with already adsorbed corrosive ions [59].

## **THIOUREA DERIVATIVES AS CORROSION INHIBITOR**

Thiourea is a good inhibitor for aluminium, whereas it has no effect on zinc and accelerates the dissolution of cadmium [60]. Evaluation of the effect of thiourea, phenyl thiourea [PTU] and 4-carboxy phenyl thiourea [CPTU] on aluminum in different concentrations of sodium hydroxide [NaOH] solution was calculated by weight loss measurements. Observation shows that the corrosion of aluminum in NaOH solution was considerably reduced in presence of such inhibitors. Thiourea forms a protective film on the surface of metal through adsorption; however the inhibition efficiency decreased with increase in NaOH concentration [61].

Electrochemical behavior of mild steel in naturally aerated 0.5 M  $H_2SO_4$  acid containing different concentrations of Acetyl thiourea chitosan polymer [ATUCS] was studied by potentiodynamic polarization, electrochemical impedance spectroscopy [EIS] measurements and surface examination via scanning electron microscope [SEM] technique. The results of EIS showed that the resistance [ $R_t$ ] increases slightly with increasing immersion time indicating a slight decrease in corrosion rate of the steel with time. Also, the corrosion rate increases with either increasing temperature or decreasing the polymer concentration as observed by polarization technique [62]. The high efficiency of thiourea in the corrosion of iron and its N-substituted derivatives under low concentration using semi empirical molecular orbital theory is attributed to strong adsorption of molecular species through the active center C-S bond. The protonation process appeared to be the effective parameter at high concentration with lowering of the inhibition efficiency of the thiourea. Alkyl N-substituted thiourea with the least protonation and with the maximum adsorption is a better inhibitor than thiourea and aryl N-substituted TU [63].

The protonation process is controlled by the charge density on the sulphur atom, lengthening and weakening of the C-S bond and the reactivity of the molecule. The effect of protonation increases with increasing concentration of TU. Substitution of the H-atom of the  $-NH_2$  group in the parent compound thiourea affects the metal-sulphur interaction, protonation, the steric and electronic factors of the substituent's change of the adsorption characteristics [63]. The inhibiting action of these organic compounds is usually attributed to interactions with metallic surfaces by adsorption.

The transition of metal/solution interface from a state of active dissolution to the passive state is attributed to the adsorption of the inhibitor molecules and the metal surface, forming a protective film. The rate of adsorption is usually rapid and hence, the reactive metal surface is shielded from the aggressive environment [64]. Adsorption process can occur by electrostatic forces between ionic charges or dipoles of the adsorbed species and the electric charge on the metal surface can be expressed by its potential with respect to the zero charge potential [ $\zeta$ ] [65]. Also, the inhibitor molecules can be adsorbed to the metal surface via the electron transfer from the adsorbed species to the vacant electron orbital of low energy in the metal to form a coordinate type of link [66]. Adsorption of inhibitor molecules is often a displacement reaction involving removal of adsorbed water molecules from the metal surface. The adsorption of the inhibitor molecules on the metal surface and the change in the interaction energy with water molecules in passing from the dissolved to the adsorbed state form an important part of the free energy change of adsorption process.

The inhibitive action of thiourea on the corrosive behavior of Armco iron was investigated in deaerated 0.5M HCl solution by means of potentiodynamic and electrochemical impedance spectroscopy techniques. The inhibitor effectiveness increases with its concentration, reaches a maximum [at about 1 mM] and then decreases. The adsorptive behaviour of thiourea on the electrode surface up to its peak follows a Frumkin-type isotherm with lateral repulsion, where the molecules are vertically adsorbed on the iron surface via sulphur atom. Thiourea acts as a mixed inhibitor up to the critical concentration, decreasing dissolution of iron and hydrogen evolution reaction by blocking the electrode surface [67].

Ditoyl thiourea [DTTU] showed very good inhibition efficiency [IE] on the corrosion of mild steel in 20% formic acid by weight loss and potentiodynamic polarization methods. The IE varied with the concentration of the compounds, solution temperature, immersion time and concentration of the acid solution. Adsorption of the acid on the steel surface was observed to obey Temkin's adsorption isotherm. The values of activation energy and free energy of adsorption indicated physical adsorption of these compounds on the steel surface while the potentiodynamic polarization studies revealed that these compounds are mixed type inhibitors. The presence of thiourea derivative lowers corrosion rate [ $I_{\text{corr}}$ ] and inhibit corrosion by blocking the active sites of the metal [68].

Corrosion inhibition of thiourea derivatives was further confirmed by Subramanyama [69] who investigated the effect of phenyl thiourea [PTU], diphenyl thiourea [DPTU], allyl thiourea [ATU], *p*-tollyl thiourea [p-TTU] and *N,N*-dimethyl thiourea [DMTU] on the corrosion of aluminium in sodium nitrite solution at 303 K. A significant decrease in the corrosion rate of aluminium was observed by the presence of traces of these compounds. All the inhibitors follow the Frumkin adsorption isotherm. The results indicate that these compounds act as cathodic inhibitors. The negative values of free energy of adsorption and high degree of protection also confirm the strong interaction of these compounds on the corroding aluminum surface.

Analysis of the inhibiting effect of dicyclohexyl thiourea [DCTU] on the corrosion behavior of 304L stainless steel in 2 M hydrochloric acid solution indicates that DCTU acted as an efficient anodic inhibitor for the corrosion of 304L SS. Excellent inhibition performance was evident and found to vary with temperature and concentration of the inhibitor, however the inhibition was due to chemisorption mechanism. The deduced thermodynamic parameters of adsorption revealed a strong interaction and spontaneous adsorption of DCTU on the metal surface [70]. These results correlates with the observation of the inhibition action of *N*-cyclohexyl-*N*-phenyl thiourea [CPTU] on the corrosion behaviour of 304 stainless steel in 3M hydrochloric acid solution using potentiodynamic polarization technique and the results obtained reveal CPTU to act as an efficient anodic inhibitor for the corrosion of 304 stainless steel. Good inhibition efficiency was evident in the acidic solution, and it was found to vary with temperature and concentration of the inhibitor. The adsorption of this compound on the 304 stainless steel surface was found to obey the Temkin adsorption isotherm, and the inhibition was governed by physical adsorption mechanism.

*N*-[2-thiophenyl]-*N'*-phenyl thiourea [TPTU] proves to be an excellent inhibitor in the corrosion behavior of mild steel in 0.05 M and 0.1M HCl, 0.025 M and 0.05 M H<sub>2</sub>SO<sub>4</sub> solutions with potentiodynamic polarization technique. The results obtained reveal that TPTU is an efficient anodic inhibitor in the acid environment and is more effective in reducing corrosion of mild steel in HCl than in H<sub>2</sub>SO<sub>4</sub> media. The deduced thermodynamic parameters of adsorption reveal a strong interaction and spontaneous adsorption of TPTU on the mild steel surface [71].

The corrosion inhibition of stainless steel [430] by thiourea in 0.5 M H<sub>2</sub>SO<sub>4</sub> was studied at room temperature, using weight loss and electrochemical [AC impedance and Tafel polarization] techniques. Potentiodynamic polarization study represents this inhibitor as having cathodic and anodic nature, and changes in Tafel and impedance parameters [I<sub>corr</sub>, R<sub>ct</sub> & C<sub>dl</sub>], indicate the absorbed protective film grows with increasing concentration of inhibitor. Result shows this inhibitor to perform well as corrosion inhibitor for Ferritic stainless steel [72].

### **THIADIAZOLE DERIVATIVES AS CORROSION INHIBITOR**

Bentiss et al [73, 74] used the weight loss, electrochemical impedance spectroscopy [EIS], XPS, and theoretical computation methods to study the mechanism of corrosion inhibition of 1, 3, 4-thiadiazole derivatives on mild steel [MS] in different acidic solutions [75-77]. Solmaz et al. reported the adsorption properties and corrosion inhibition of 2-amino-5-mercapto-1,3,4-thiadiazole [AMT] and 2-mercapto-thiazoline [2MT] on MS in hydrochloric acid, respectively. Yadav et al. investigated the inhibition of copper corrosion in 3.5% NaCl solution with and without 2, 5-dimercapto-1, 3, 4-thiadiazole [DMTD] by means of the weight loss method and electrochemical technique [78]. The effect of 2, 5-dimercapto-1, 3, 4-thiadiazole [DMTD] on the corrosion of mild steel [MS] in dilute tetraoxosulphate (vi) acid (H<sub>2</sub>SO<sub>4</sub>) revealed the mixed-type inhibitive nature of thiadiazole without change of the mechanism of hydrogen evolution. The inhibition efficiency increased with the increase in concentration of DMTD but decreased with the increase of temperature. Adsorption of the inhibitor on the MS surface obeyed the Langmuir adsorption isotherm [79].

N-[4-phenyl-5-[p-tolylimino]-4,5-dihydro-1,3,4-thiadiazole-2-yl] benzamide, 2-acetyl-4-phenyl-5-[p-tolylimino]-4,5-dihydro-1,3,4-thiadiazole and Ethyl-4-phenyl-5-[p-tolylimino]-4,5-dihydro-1,3,4-thiadiazole-2-carboxylate were synthesized and used as additives to protect grade 1018 carbon steel in naturally aerated NaCl solution using open circuit potential [OCP], potentiodynamic polarization and electrochemical impedance spectroscopy [EIS] complemented by surface examination via scanning electron microscope [SEM]. Results showed the inhibitor to be anodic-type inhibitors, where the corrosion rate decreases with increase in the inhibitor concentration [80]. The influence of 2-amino-1,3,4-thiadiazole [AT], 5-methyl-2-amino-1,3,4-thiadiazole [MAT], 5-ethyl-2-amino-1,3,4-thiadiazole [EAT] and 5-propyl-2-amino-1,3,4-thiadiazole [PAT] on the inhibition of corrosion of mild steel [MS] in hydrochloric acid was investigated by weight loss and potentiodynamic polarization techniques. The inhibition efficiency [IE] of these compounds was found to vary with the inhibitor concentration, immersion time, acid concentration and solution temperature. The thiadiazole derivatives exhibited good inhibition efficiency [IE] for mild steel in hydrochloric acid solution [81].

According to Liu et al [82] these organic compounds inhibit the corrosion of mild steel by adsorption on the metal-solution interface thereby creating a barrier that prevents the active ions in the corrosion reactions to get to the surface. Synthesized substituted 1, 3, 4-Thiadiazol-2-amines exhibited good corrosion inhibition of mild steel in H<sub>2</sub>SO<sub>4</sub> due to coverage of the metal surface by the inhibitor molecules, thus preventing contact of the corroding acid species [83]. Rafiquee et al [84] studied the effect of 2-amino-1, 3, 4-thiadiazoles [AT], 2-amino-5-methyl-1, 3, 4-thiadiazoles [AMT], 2-amino-5-ethyl -1, 3, 4-thiadiazoles [AET] and 2-amino-5-propyl -1, 3, 4-thiadiazoles [APT] on the corrosion of mild steel in formic acid and acetic acid by weight loss, potentiodynamic polarization and electrochemical impedance techniques. The inhibition efficiency of these compounds was found to vary with the inhibitor concentration, immersion time, temperature and acid concentration.

Investigation of the effect of N-[4-phenyl-5-[p-tolylimino]-4, 5-dihydro-1, 3, 4-thiadiazole-2-yl] benzamide, 2-acetyl-4-phenyl-5-[p-tolylimino]-4,5-dihydro-1,3,4-thiadiazole, Ethyl-4-phenyl-5-[p-tolylimino]-4,5-dihydro-1,3,4-thiadiazole-2-carboxylate, 2-benzoyl-4-phenyl-5-[p-tolylimino]-4,5-dihydro-1,3,4-thiadiazole, 2-benzoyl-4-phenyl-5-[4-bromophenylimino]-4,5-dihydro-1,3,4-thiadiazole, 2-benzoyl-4-[p-tolyl]-5-[p-tolylimino]-4,5-dihydro-1,3,4-thiadiazole on the inhibition of C-steel corrosion by some thiadiazole derivatives in H<sub>2</sub>SO<sub>4</sub> was investigated by weight loss, potentiodynamic polarization, linear polarization resistance [LPR] and electrochemical impedance spectroscopy [EIS] techniques. The presence of these compounds in the solution was found to decrease the double layer capacitance, increase the charge transfer resistance and increase linear polarization. Polarization studies showed that all the compounds studied to be mixed type inhibitors with a slight predominance of cathodic character [85].

According to Ashish et al [86] bis-thiadiazole derivatives [BTDs] exhibited >90% inhibition efficiency at concentration as low as 40 ppm against the corrosion of mild steel in dilute HCl solution using weight loss, electrochemical impedance spectroscopy [EIS] and potentiodynamic polarization methods. Polarization curves indicate that they are mixed type of inhibitors.

Lebrini et al [87] investigated the inhibitive action of some thiadiazole derivatives, namely 2,5-bis[2-thienyl]-1,3,4-thiadiazole [2-TTH] and 2,5-bis[3-thienyl]-1,3,4-thiadiazole [3-TTH] against the corrosion of mild steel in dilute H<sub>2</sub>SO<sub>4</sub> solution using weight loss measurements, Tafel polarisation and electrochemical impedance spectroscopy [EIS] techniques. Results revealed that these compounds inhibited the steel corrosion in acid solution with the protection efficiency increasing with increase in inhibitor concentration. The ability of the molecule to adsorb on the steel surface was dependent on the position of the sulphur atom on the thienyl substituent.

The inhibition properties of 2,5-bis[n-pyridyl]-1,3,4-thiadiazoles [n-PTH] on corrosion of mild steel in different acidic media [1 M hydrochloric acid (HCl), 0.5 M tetraoxosulphate (vi) acid (H<sub>2</sub>SO<sub>4</sub>) and 1 M perchloric acid (HClO<sub>4</sub>)] was analyzed by electrochemical impedance spectroscopy [EIS]. The n-PTH derivatives exhibit good inhibition properties in different acidic solutions and the calculated values of the free energy of adsorption ( $DG_{ads}$ ) revealed the adsorption mechanism of [n-PTH] on steel surface is mainly due to chemisorption [88]. The effect of inhibitors adsorbed on metallic surfaces in acid solutions, is to slow down the cathodic reaction as well as the anodic process of dissolution of the metal. Such effect is obtained by forming a barrier of diffusion or by means of the blockage of the reaction sites [89]. The nitrogen, oxygen and sulphur atoms of the inhibitor molecules of thiadiazole derivatives allowed it to be adsorbed readily on the metal surface forming an insoluble stable film on the metal surface thus decreasing metal dissolution. Molecular adsorption on the metal surface is due to coordination of the electron. Maximum efficiency of the investigated inhibitors was observed even at a very low concentration; however rate of corrosion increases with rise in temperature.

## Conclusion

The main methods for corrosion protection are through inhibitors. A number of green alternatives to chromates are currently emerging, oriented primarily towards minimizing environmental impact and, secondarily, towards providing effective corrosion inhibition. From the comprehensive review of the literature presented in this article, thiourea and thiadiazole-based compounds seem to fulfill the basic requirements to be considered as a component of more environmentally-friendly formulations: low toxicity and acceptable inhibition power.

In relation to the corrosion protection of metal alloys by these compounds, most of the recently published studies have focused on the study of their behaviour as inhibitors in aqueous solutions and various authors have shown that these compounds are effective inhibitors against uniform and pitting corrosion in aqueous environments from tests with several ferrous alloys. These compounds show efficiency similar to that obtained using classical Cr (VI) based inhibitors.

Dealing with the inhibition mechanism, results obtained in the study of different systems suggest that these compounds behave as mixed type inhibitors depending on the environment. They act by blocking the active sites in the metallic alloys. During the inhibition process, protective surface films through adsorption are formed, thus the need to focus future research and development of new high-performance and environmentally-friendly thiourea and thiadiazole compounds on ferrous alloys.

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