

## CHAPTER - 2

### REVIEW OF LITERATURE

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#### 2. 1 Introduction

Mild steel is an iron-carbon alloy containing less than 0.25 percent carbon which makes it more ductile and less hard thus rendering it unsuitable for structural work. Besides carbon, there are many metal elements that are a part of steel alloys. The elements other than iron and carbon, used in steel are chromium, manganese, tungsten and vanadium. All these elements along with carbon, act as hardening agents as they prevent dislocations from occurring inside the iron crystals and prevent the lattice layers from sliding past each other. Varying the amounts of these hardening agents creates different grades of steel. The amount of carbon is a deciding factor, which decides hardness of the steel alloy.

A steel alloy with high carbon content is mild steel, which is in fact much harder and stronger than iron. Though increased carbon content increases the hardness of the steel alloy, it causes a decrease in its ductility. Steel is very important in our day-to-day life, starting from the steel cookwares to scientific instruments like scalpel. Due to its cost-effectiveness and strength, steel is used in engineering works and in infrastructure developments such as roads, railways, bridges, buildings and stadiums. The ferromagnetic properties of mild steel make it ideal for manufacture of electrical devices and motors. Growth and development of the steel industry marks the economic progress of the country. Several works have been done with compounds containing polar functions on the corrosion inhibition of mild steel in various aqueous media.

Overview of the chemical abstracts provides valuable insight into the extent and nature of corrosion studies undertaken in this field. In recent years, the practice of corrosion inhibition has become more oriented towards healthy and safety considerations. Consequently greater research efforts have been directed towards formulating environmentally acceptable organic compounds containing heteroatoms to prevent corrosion of metals.

Heterocyclic compounds containing N, O and S are considered to be effective corrosion inhibitors. The previous work done with nitrogen, oxygen and sulphur heterocycles have been analyzed and reviewed under the following topics.

- Heterocyclic corrosion inhibitors in acidic media
- Quantum chemical studies and corrosion inhibition studies

**Bentiss *et al.***, studied the relationship between electronic parameters of aromatic corrosion inhibitors and inhibition efficiency. Oxadiazole, thiadiazole and triazole derivatives have been investigated as new classes of molecules. The corrosion behaviour of mild steel in 1M HCl solution in the absence and presence of heterocyclic derivatives was investigated by the electrochemical impedance spectroscopy. The investigated results confirmed that planar (unsaturated) molecules are more efficient than partially saturated derivatives<sup>1</sup>.

**Abdel-Rehim *et al.***, studied the corrosion behaviour of 1H-pyrazole derivative (PA) on corrosion of pure iron in 1M HCl. The behaviour of this compound has been determined by electrochemical methods. The adsorption of PA on the iron surface was found to obey Langmuir adsorption isotherm. The results suggested that PA behaved mainly as an anodic inhibitor<sup>2</sup>.

**Eddy *et al.***, investigated the corrosion inhibition potential of (2s,5s,6r)-6-(2-(aminomethyl)-5-(3-(2-chlorophenyl)isoxazol-5-yl)benzamido)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid (AMPX) for mild steel in sulphuric acid using experimental (gravimetric, gasometric and thermometric methods) and quantum chemical methods. Semi empirical, Fukui, Huckel charge and other quantum chemical indices were used to study the mechanism of inhibition, possibility of protonation and interaction. The energy of interaction and proton affinity for all possible adsorption sites in AMPX has been calculated. It was found to be an excellent inhibitor and was spontaneously adsorbed on mild steel surface *via.*, amide nitrogen. Enhancement in inhibition efficiency of AMPX was observed on addition of potassium halides due to synergism<sup>3</sup>.

**Chitra *et al.***, synthesized and evaluated quinoxaline derivatives for the corrosion inhibition of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> by electrochemical and non-electrochemical methods. The results obtained by the above techniques showed that

quinoxazolines were efficient corrosion inhibitors. Tafel polarization studies revealed that quinoxazolines behaved as mixed type but anodic effect was more pronounced. The adsorption of these quinoxazoline derivatives obeyed Langmuir adsorption isotherm. The synergistic effect was found to increase in the order<sup>4</sup>  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ .

**Atta *et al.***, investigated the electrochemical corrosion behaviour and hydrogen evolution reaction of 316L stainless steel in 0.5M sulfuric acid solution containing four novel organic inhibitors using potentiodynamic polarization, electrochemical impedance spectroscopy and scanning electron microscopy techniques. The inhibition efficiency for the active centres of the four compounds was found to increase in the order  $-\text{Cl} > -\text{Br} > -\text{CH}_3 > \text{OCH}_3$ . The corrosion rate and hydrogen evolution using the compounds with methoxy group was found to increase with either increasing temperature or decreasing its concentration as observed by polarization technique and combined by EIS measurements. The compound with methoxy group had very good inhibition efficiency of 98.3% in 0.5M sulfuric acid. EIS results were confirmed by surface examination<sup>5</sup>.

**Khaled *et al.***, studied the corrosion inhibition characteristics of 1-methyl pyrazole (MPA) in hydrochloric acid media by potentiodynamic polarization and electrochemical impedance spectroscopy. Polarization studies revealed that MPA acted mainly as an anodic inhibitor in HCl. The adsorption of MPA from HCl solutions on the iron surface obeyed Temkin adsorption isotherm. The presence of lone pairs and  $\pi$  electrons of the MPA compound enhanced the inhibitory effect<sup>6</sup>.

**Ahmed Y. Musa *et al.***, examined the inhibitive action of purpald (4-amino-3-hydrazino-5-mercapto-1,2,4-triazole, 4-amino-5-hydrazino-1,2,4-triazole-3-thiol) towards the corrosion of mild steel in 2.5M  $\text{H}_2\text{SO}_4$  by electrochemical methods. The results obtained from polarization techniques were comparable with those obtained by impedance measurements. At very low concentration ( $4 \times 10^{-4}$  M) purpald attained a maximum efficiency of 95 % at 30° C. The adsorption mechanism was a combination of both physisorption and chemisorption. Polarization curves showed that purpald behaved as a mixed-type inhibitor<sup>7</sup>.

**Fekry *et al.***, have investigated the electrochemical corrosion rate and hydrogen evolution behaviour on mild steel in 0.1M sulphuric acid solution by newly synthesized

heterocyclic organic inhibitors namely 4-methyl-6-methylsulfanyl-[2,3']bipyridinyl (I), 3-(6-(methylthio)-4-phenylpyridin-2-yl)pyridine (II) and 3-(6-(methylthio)-4-(thiophen-2-yl)pyridin-2-yl)pyridine (III). The results showed that total resistance value ( $R_T$ ) or the relative thickness ( $1/C_T$ ) value increases with increasing inhibitor concentration. The decrease in the corrosion or hydrogen evolution rate of the mild steel followed the order  $I < II < III$ . The impedance measurement results were confirmed by surface examination using scanning electron microscope<sup>8</sup>.

**Singh *et al.***, have reported the corrosion inhibition properties of ceftadizime (CZD) for mild steel corrosion in 0.5M  $H_2SO_4$  using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and weight loss techniques. They found that CZD was found to be an effective inhibitor. Potentiodynamic studies revealed that CZD acted as a mixed-type inhibitor. The results obtained from Tafel polarization method showed good agreement with the results obtained from EIS. Mixed mode of adsorption was found for corrosion inhibition and the adsorption process followed Langmuir isotherm<sup>9</sup>.

**Donor *et al.***, reported the inhibitive action of 2-amino-5-mercapto-1,3,4-thiadiazole (2A5MT) and 2-mercaptothiazoline (2MT) on mild steel corrosion in 1M  $H_2SO_4$  by potentiodynamic polarization, linear polarization resistance and electrochemical impedance spectroscopic techniques. Potentiodynamic polarization curves indicated that 2A5MT and 2MT acted as mixed type inhibitors. Both the inhibitors showed excellent performance in the acid media. SEM and AFM micrographs study showed that the reported inhibitors form a good protective film on the steel surface. The experimental results were substantiated by theoretical calculations<sup>10</sup>.

**Obi-Egbedi *et al.***, investigated the inhibition properties, thermodynamic and quantum chemical studies of alloxazine on mild steel corrosion in  $H_2SO_4$  using weight loss and computational techniques. Adsorption of the inhibitor followed Temkin's model and first order kinetics. Both activation and thermodynamic parameters were calculated. DFT studies explained the mechanism of inhibitor action<sup>11</sup>.

**Bentiss *et al.***, studied the relationship between corrosion inhibiting effect and molecular structure of 2,5-bis (n-pyridyl)-1,3,4-thiadiazole derivatives in acidic media (1M HCl, 0.5M  $H_2SO_4$  & 1M  $HClO_4$ ) using a.c impedance and DFT studies. Calculated

values of free energy revealed chemisorptive nature for the studied compound. Quantum chemical calculations and experimental inhibition efficiency were correlated. The inhibition effect was explained in terms of electronic properties<sup>12</sup>.

**Kara *et al.***, employed density functional theory and ab initio methods on four isoxazoline derivatives. Isoxazoline derivatives were found to be good corrosion inhibitors in aqueous acidic oil medium. The corresponding structures have been optimized and some quantum chemical parameters were calculated using the DFT/B3LYP and HF methods with the 6-31G(d,p) basis set and found the relationship between the molecular structure and their inhibition efficiencies<sup>13</sup>.

**Shukla *et al.***, synthesized and studied the corrosion behaviour of mild steel in 1N HCl in the presence of five triazine derivatives namely hexahydro-1,3,5-triphenyl-S-triazine (Inh-1), hexahydro-1,3,5-p-tolyl-S-triazine (Inh-2), hexahydro-1,3,5-p-methoxyphenyl-S-triazine (Inh-3), hexahydro-1,3,5-p-aminophenyl-S-triazine (Inh-4), hexahydro-1,3,5-p-nitrophenyl-S-triazine (Inh-5) using weight loss, polarization resistance, Tafel polarization and electrochemical impedance spectroscopy techniques. All the triazine derivatives showed highest inhibition efficiency at 300 ppm concentration. At optimum concentration, the order of inhibition efficiency was found to be Inh-4 > Inh-3 > Inh-2 > Inh-1 > Inh-5. All the triazines were found to obey Langmuir adsorption and acted as mixed inhibitors. Thermodynamic parameters were calculated to know the mechanism of corrosion inhibition. The impedance study gave the same efficiency trend as found in weight loss, polarization resistance and Tafel polarization methods. Atomic force microscopy (AFM) was used to know the surface roughness of the mild steel<sup>14</sup>.

**Abdel Hameed *et al.***, studied the corrosion inhibition of 5-chloro-1-phenyl-3-methylpyrazolo-4-methinethiosemicarbazone (PS) towards carbon steel in 1M HCl using chemical and electrochemical techniques. The effect of temperature on the rate of corrosion and other thermodynamic parameters were computed. Polarization curves showed inhibition was of mixed type, but predominantly under cathodic control. Surface morphology of the corroded surface was studied by SEM<sup>15</sup>.

**Aderdour *et al.***, synthesized inhibitors namely 3,7-dimethylquinoxalin-2(1H)-one ( $\text{CH}_3\text{-Q=O}$ ) and 3,7-dimethylquinoxalin-2(1H)-thione ( $\text{CH}_3\text{-Q=S}$ ) and have

evaluated their inhibitive performance for mild steel corrosion in 0.5M H<sub>2</sub>SO<sub>4</sub> by weight loss, polarization curves and EIS measurements. Polarization studies revealed that CH<sub>3</sub>-Q=O acted as cathodic and CH<sub>3</sub>-Q=S as mixed type of inhibitors. The results obtained from chemical and electrochemical measurements confirmed CH<sub>3</sub>-Q=S performed better and adsorption followed Langmuir isotherm<sup>16</sup>.

**Chakravarthy *et al.***, have synthesized isonicotinic acids (1H-indol-3-yl-methylene)hydrazide (INIMH) and (1H-pyrrol-2-yl-methylene)hydrazide (INPMH) and evaluated their inhibitive characteristics for mild steel corrosion in 0.5M HCl using mass loss and electrochemical techniques. The synthesized inhibitors were characterized by FTIR, <sup>1</sup>H-NMR and mass spectral studies. Potentiodynamic polarization studies revealed that the investigated compounds behaved as mixed-type. The adsorption process obeyed Langmuir isotherm model and various thermodynamic parameters were evaluated<sup>17</sup>.

**Tripati *et al.***, have studied the inhibition efficiency of newly synthesized pyridyl substituted thiourea compounds namely 1-(2,6-diazene)-3-benzyl thiourea (ST<sub>1</sub>), 1-(3'-pyridyl)-3-benzyl thiourea (ST<sub>2</sub>), 1-(3'-pyridyl)-1-phenyl thiourea (ST<sub>3</sub>), 1-(2'-pyridyl)-3-phenyl thiourea (ST<sub>4</sub>) for mild steel corrosion in HCl and H<sub>2</sub>SO<sub>4</sub> solution. In both the methods, it was shown that the results of inhibition efficiency of (ST<sub>1</sub>, ST<sub>2</sub>, ST<sub>3</sub>, ST<sub>4</sub>) increased with increasing concentrations of the inhibitor and also increased with increasing concentrations of both the acids. Maximum inhibition efficiency was 99.26 % in 2.5N H<sub>2</sub>SO<sub>4</sub> and 98.48 % in 2.5N HCl. The synthesized pyridyl substituted thioureas were efficient corrosion inhibitors for mild steel in H<sub>2</sub>SO<sub>4</sub> and HCl<sup>18</sup>.

**Obot *et al.***, evaluated the corrosion inhibition efficiency of sulphathiazole (STZ) for mild steel corrosion in 0.5M HCl at 303 - 333 K using gravimetric and quantum chemical methods. The obtained results proved that STZ was a very good inhibitor, even at very low concentrations. The adsorption on steel surface obeyed Temkin adsorption isotherm. They proposed chemisorption mechanism and adsorption on steel surface was a spontaneous process. The kinetic and thermodynamic parameters for mild steel corrosion and inhibition by adsorption were discussed. An attempt was made to correlate the inhibitive action of STZ with theoretical results. Quantum chemical calculations showed that STZ adsorbed mainly on active centres such as nitrogen, oxygen and some carbon atoms<sup>19</sup>.

**Kabanda *et al.***, have investigated some heterocyclic structures and molecular properties of selected triazole and benzimidazole derivatives namely 2-aminobenzimidazole (ABI), 1,3-benzothiazole (BTH), benzotriazole (BTA), 2-methyl benzimidazole (MBI), 2-(2-pyridyl)benzimidazole (PBI), 2-(aminomethyl)benzimidazole (AMBI), 5-amino-3-mercapto-1,2,4-triazole (5AMTZ), 2-hydroxybenzimidazole (HBI), benzimidazole (BI) and 5-amino-1,2,4-triazole using density functional theory (DFT) method, performed with three different basis sets (6-31(d,p), 6-31+(d,p) and 6-311G(d,p) to determine their reactive centres which might get adsorbed onto the metal surface. The results showed that protonated species have less charge density than the non-protonated species. The protonated species interacted with the metal surface through physisorption mechanism whereas non-protonated species interacted through chemisorption mechanism. Quantitative structure activity relationship approach was used to correlate quantum chemical parameters with the experimentally determined inhibition efficiency<sup>20</sup>.

**Harikumar *et al.***, investigated the corrosion behaviour of mild steel in 1M sulphuric acid in the presence of Amoxicillin inhibitor using weight loss, electrochemical techniques, hydrogen permeation and diffuse reflectance spectroscopic measurements. The results obtained from all these techniques revealed that inhibition efficiency increased with increase in the concentration of the inhibitor. Surface morphology of the corroded specimen was studied by scanning electron microscopy. Potentiodynamic polarization studies indicated that Amoxicillin acted as mixed-type inhibitor. The adsorption of inhibitor obeyed Langmuir adsorption isotherm. Quantum chemical calculations were computed and discussed<sup>21</sup>.

**Wang *et al.***, explored the influence of chloride ion on the corrosion inhibition of 1,4-bis(benzimidazolyl)butane (BBB) in 0.25M H<sub>2</sub>SO<sub>4</sub> using weight loss, electrochemical methods and discussed the synergistic inhibition mechanism. The results revealed that BBB together with chloride ion was more effective than single BBB for mild steel corrosion. Polarization curves showed that single BBB and BBB-NaCl mixture were mixed type inhibitors. The adsorption of BBB-NaCl mixture was stronger than that of BBB and obeyed Langmuir adsorption isotherm. The results obtained from weight loss and electrochemical results were in good agreement<sup>22</sup>.

**Manimegalai *et al.***, investigated the inhibiting performance of Trazodone (Tz) on mild steel in 1M HCl using weight loss measurements. The effect of immersion time was also studied. They found that maximum inhibition efficiency of 96 % was achieved and showed that Tz was an excellent inhibitor. Tz followed Langmuir adsorption isotherm. The mechanism of corrosion inhibition was also proposed<sup>23</sup>.

**Wang *et al.***, tested the inhibitive effect of 1,4-bis (benzimidazolyl) benzene (BBMB) on the corrosion of mild steel in 0.5M HCl and 0.25M H<sub>2</sub>SO<sub>4</sub> by weight loss and electrochemical techniques. The results showed that BBMB was found to be a good inhibitor in both acids. Maximum inhibition efficiency was observed in HCl than that in H<sub>2</sub>SO<sub>4</sub>. The adsorption of the inhibitor on mild steel surface was found to be spontaneous and followed both physisorption and chemisorption. The adsorption of this compound was found to obey Langmuir adsorption isotherm in both the acids. Polarization studies revealed that BBMS acted as mixed type inhibitor<sup>24</sup>.

**Fouda *et al.***, investigated the inhibitive action of some phenolic derivatives such as 4-(5-(4-dimethylamino)phenyl)-1H-pyrazol-5-yl)phenol (compound A) and 4-(5-(4-nitrophenyl)-1H-pyrazol-5-yl)phenol (compound B) on the corrosion of mild steel in 1M HCl solution. Electrochemical impedance spectroscopy, potentiodynamic polarization, scanning electron microscope technology with energy dispersive X-ray spectroscopy (SEM-EDS) and weight loss methods were used to study the inhibition action at 30°C. The order of inhibition efficiency was found to be compound A > compound B. The electrochemical results confirmed that these compounds were efficient inhibitors for mild steel and exhibited a maximum efficiency of 85% at 30°C. Polarization curves indicated that these inhibitors were of mixed type. The adsorption of these phenolic derivatives obeyed Frumkin adsorption isotherm and kinetic parameters were calculated and discussed<sup>25</sup>.

**Kara *et al.***, performed quantum chemical calculations using density functional theory (DFT) and ab initio (HF) methods. Relationship between molecular structure and their inhibition efficiencies were performed on isoxazoline and isoxazolidine derivatives. The inhibition efficiency increased with the increase in dipole moment and  $\Delta N$ . Due to the presence of second benzene ring in isoxazolidine derivatives, the inhibition efficiency of isoxazolidine was found to be higher than isoxazoline derivatives<sup>26</sup>.



**Ghazoni et al.**, investigated two novel pyridazine derivatives namely ethyl (6-oxo-3-phenylpyridazin-1(6H)-yl) acetate (GP<sub>2</sub>) and ethyl (3-phenyl-6-thioxopyridazin-1(6H)-yl) acetate (GP<sub>3</sub>) as corrosion inhibitors for C38 steel in 1M HCl. A comparative statement was made using gravimetric measurements, potentiodynamic polarization methods and electrochemical impedance spectroscopy techniques based on inhibition efficiencies. Effect of temperature was studied between 308 and 343 K. In addition, thermodynamic activation parameters and adsorption parameters were determined and discussed. Polarization curves revealed that these compounds acted as cathodic/anodic inhibitors. Moreover, the results obtained by electrochemical methods were in good agreement with the results from gravimetric measurements<sup>27</sup>.

**El Ouali et al.**, investigated the inhibiting action of three pyrazole derivatives namely 1,1'-propane-1,4-diylbis[3-chloromethyl)-5-methyl-1H-pyrazole] Bip (1), dimethyl 1,1'-butane-1,4-diylbis(5-methyl-1H-pyrazole-3-carboxylate) Bip (2) and 1,1'-butane-1,4-diylbis[3-chloromethyl)-5-methyl-1H-pyrazole] Bip (3) towards the corrosion of C38 steel in 1M HCl solution. Weight loss and potentiodynamic polarization method modelled with an equivalent electric circuit were used to evaluate the inhibition efficiency of three pyrazole derivatives. Potentiodynamic polarization studies clearly revealed that they behave predominantly as cathodic type. The adsorption obeyed Langmuir adsorption isotherm. Thermodynamic parameters were investigated at different concentrations and temperature. Different quantum chemical parameters such as  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$  and energy gap  $\Delta E$  were calculated by considering the density functional theory (DFT) using the GAUSSIAN O3W suite of programs<sup>28</sup>.

**Scendo et al.**, studied the inhibitory effect of N-(2-chloro benzylidene)-4-acetylaniline (CBAA) on the corrosion of St3S carbon steel in 1.2M HCl solution at different temperatures using weight loss, Tafel polarization techniques, scanning electron microscopy and quantum chemical method. In weight loss studies, zero order kinetics was followed for the CBAA compound. The adsorption of CBAA was found to obey Langmuir isotherm at all the studied temperatures. The kinetic and thermodynamic parameters were determined and discussed. Quantum chemical parameters confirmed the adsorption of CBAA molecule on the steel surface on the basis of donor-acceptor interactions<sup>29</sup>.

**Junaedi *et al.***, synthesized and investigated the corrosion inhibitory effects of 1,5-dimethyl-4-((2-methylbenzylidene)amino)-2-phenyl-1H-pyrazol-3(2H)-one (DMPO) on mild steel in 1M HCl using electrochemical impedance spectroscopy, potentiodynamic polarization, open circuit potential and electrochemical frequency modulation. DMPO was found to be an efficient inhibitor and it exhibited maximum inhibition efficiency of 87%. The adsorption on mild steel surface obeyed Langmuir adsorption isotherm. The correlation between the quantum chemical parameters and inhibition efficiencies of DMPO was investigated using DFT calculations<sup>30</sup>.

**Obi-Egbedi *et al.***, explored the use of xanthione as corrosion inhibitor for mild steel surface in sulphuric acid solution using gravimetric and UV-visible spectrophotometric methods. The effects of temperature on corrosion and inhibition processes have been discussed. Xanthione was found to be a good inhibitor at very low concentration. Some thermodynamic parameters were thoroughly assessed and computed. A UV-visible spectrum was used to reveal the formation of inhibitor-Fe complex. Quantum chemical calculations were correlated with the inhibitive effect of Xanthione and indeed both the calculations were in excellent agreement<sup>31</sup>.

**Yadav *et al.***, synthesized some benzimidazole derivatives namely 4-(phenyl)-5-[(2-methyl-1H-benzimidazole-1-yl)methyl]-4H-1,2,4-triazole-3-thiol (Inh I), 4-(4-methylphenyl)-5-[(2-methyl-1H-benzimidazole-1-yl)methyl]-4H-1,2,4-triazole-3-thiol (Inh II), 4-(4-methoxyphenyl)-5-[(2-methyl-1H-benzimidazole-1-yl)methyl]-4H-1,2,4-triazole-3-thiol (Inh III) and studied their corrosion inhibitive properties for mild steel in 15% HCl by weight loss and electrochemical techniques. They investigated the effect of temperature and discussed some thermodynamic parameters for corrosion inhibition. In polarization studies, all the investigated inhibitors behaved as mixed type but predominantly under anodic control. The experimental inhibition efficiencies were consistent with theoretical studies<sup>32</sup>.

**Jannathul Firdhouse *et al.***, have been investigated the inhibition of mild steel corrosion by 5'-phenyl-2',4'-dihydrospiro[indole-3,3'-pyrazol]-2(1H)-one (SPA) in 1M HCl and 0.5M H<sub>2</sub>SO<sub>4</sub> using weight loss, electrochemical techniques and quantum chemical studies. Weight loss studies have shown that SPAH effectively inhibited the corrosion of mild steel in 1M HCl and 0.5M H<sub>2</sub>SO<sub>4</sub> media. In polarization studies, SPAH

acted as mixed type inhibitor and adsorption on mild steel surface followed Langmuir isotherm in 1M HCl and Temkin adsorption isotherm in 0.5M H<sub>2</sub>SO<sub>4</sub>. Protective film formation was confirmed by SEM. The theoretical findings correlated satisfactorily with experimental results<sup>33</sup>.

**Touir *et al.***, compared the inhibitive performance of 5-chloro-benzimidazol-2-one (B<sub>1</sub>), 5-methyl-benzimidazol-2-one (B<sub>2</sub>), benzimidazol-2-one (B<sub>3</sub>) for mild steel corrosion in 1M HCl using weight loss measurements, potentiodynamic polarization curves and electrochemical impedance spectroscopy methods. They compared the results and showed that B<sub>1</sub> was the best inhibitor. Potentiodynamic studies clearly revealed that the inhibitor B<sub>1</sub> acted as mixed type and EIS study showed the formation of a protective film. Reasonably good agreement was observed for the data obtained from weight loss measurements and electrochemical techniques<sup>34</sup>.

**Ananth Kumara *et al.***, investigated the inhibitive effect of 1-(2-methyl-4-(2-methylphenyldiazenyl) phenyl) azonaphthalen-2-ol on mild steel corrosion in sulphuric acid and the synergistic effect of iodide ions by weight loss and potentiodynamic polarization methods. Data obtained from EIS studies were analyzed to determine the inhibition process through appropriate equivalent circuit models. Inhibition efficiency obtained from the various methods was in good agreement. Electrochemical polarization results indicated that 1-(2-methyl-4-(2-methylphenyldiazenyl) phenyl) azonaphthalen-2-ol acted as mixed type inhibitor and impedance results showed that the corrosion of mild steel was mainly controlled by a charge transfer process<sup>35</sup>.

**Udhayakala *et al.***, evaluated the corrosion inhibitive performance of three phenyltetrazole substituted compounds, namely 5-phenyl-1H-tetrazole (PT), 5-p-tolyl-1H-tetrazole (M-PT) and 5-(4-methoxyphenyl)-1H-tetrazole (MO-PT) for mild steel by quantum chemical calculations based on density functional theory (DFT) method at the B3LYP/6-31G(d,P) basis set level. DFT calculations provided a good relationship between the molecular and electronic structures and inhibition efficiency. The calculated HOMO energy, energy gap ( $\Delta E$ ) and the value of dipole moment were in good correlation with the efficiency of the corrosion inhibitors. The theoretical results obtained using DFT based reactivity indexes, were found to be consistent with the experimental outcomes<sup>36</sup>.

**Ousslim *et al.***, tested three piperazine derivatives namely 1-benzyl piperazine ( $C_2$ ), 1,6-di(1-benzylpiperazine-1-carboxamide)hexane ( $C_4$ ) and bis(1-benzylpiperazine) disulfure de thiuram ( $C_5$ ) as corrosion inhibitors for mild steel corrosion in 3.2M  $H_2SO_4$ . Gravimetric, potentiodynamic polarization and electrochemical impedance spectroscopy were carried out. Potentiodynamic studies clearly revealed that all the tested inhibitors acted as mixed-type. Adsorption isotherms were fitted by Langmuir isotherm and activation parameters were estimated by studying the effect of temperature in the range 25 - 60°C. At  $10^{-3}$  M,  $C_4$  and  $C_5$  attained a maximum inhibition value of 95%. The quantum theoretical calculations were in good agreement with the result obtained from electrochemical study and the structure–corrosion protection relationship confirmed S, N and O atoms were the adsorption centres<sup>37</sup>.

**Mourya *et al.***, made a comparative study of the inhibitive characteristics of 4-(N,N-dimethylamino)benzaldehyde thiosemicarbazone (DMABT) on the corrosion of mild steel in 1N HCl and  $H_2SO_4$ . The inhibitor was investigated by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopic measurements. DMABT behaved as a mixed-type inhibitor, but predominantly acted as cathodic type. Adsorption followed Langmuir adsorption isotherm model in both the acids. At 450  $\mu$ M, DMABT was found to be an excellent inhibitor and showed maximum inhibition efficiency of 95.7 % and 97.8 % in HCl and  $H_2SO_4$  respectively. The corroded and inhibited metal surfaces have been characterized by energy dispersive X-ray (EDS), scanning electron microscopy (SEM) and atomic force microscopy (AFM). Moreover, the structural correlation of the inhibition efficiency of DMABT has been further ascertained through molecular modeling using density functional theory (DFT)<sup>38</sup>.

**Al-Amiery *et al.***, examined the inhibitory action of Schiff base derived from 4-amino antipyrine and thiosemicarbazide for the corrosion inhibition of mild steel in 1M  $H_2SO_4$  using electrochemical impedance spectroscopy, potentiodynamic polarization and electrochemical frequency modulation (EFM). The synthesized schiff base was found to be a good inhibitor even at low concentrations with 93% efficiency. Polarization studies clearly showed that it acted as mixed type. The obtained inhibition efficiencies were comparable with EIS results and moreover followed Langmuir adsorption isotherm. The effectiveness of the inhibitor was also verified by SEM<sup>39</sup>.

**Ju et al.**, have made a theoretical study on three nitrogen-bearing heterocyclic compounds as corrosion inhibitors for mild steel in acid media to determine the relationship between molecular structure of the compounds and inhibition efficiency. The structural parameters such as energy gap and energy of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), the charge distribution of the studied inhibitors, the absolute electronegative values and the fraction of electrons transferred from the inhibitors to mild steel were also calculated and correlated with inhibition efficiencies. The obtained results showed that inhibition efficiencies increased with increase in energy of  $E_{\text{HOMO}}$  and decrease in energy gap of frontier molecular orbital<sup>40</sup>.

**Gurudatt et al.**, have studied three newly synthesized pyridine based 2,5-disubstituted 1,3,4-oxadiazoles and evaluated their inhibitive performance for mild steel corrosion in 0.5M hydrochloric acid using mass loss and electrochemical techniques. Adsorption of all the three inhibitors obeyed Langmuir isotherm model. SEM - EDAX analysis proved that the protective film formed on the mild steel surface showed higher stability and low permeability in aggressive solution. Quantum chemical calculations excellently correlated with the experimental observations. Electrochemical impedance spectroscopy measurements explained the mechanism of action of inhibitors<sup>41</sup>.

**Yadav et al.**, carried out a systematic study to ascertain the inhibitive performance of some synthesized phenylazopyrimidone dyes namely 3-(p-nitrophenylazo)-4-amino-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (NABIP) and 3-(p-methoxyphenylazo)-4-amino-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (MABIP) for mild steel corrosion in 15% HCl using electrochemical measurements and quantum chemical calculations. At 303 K, the inhibitors NABIP and MABIP showed inhibition efficiencies of 93.1 and 97.9 % at 200 ppm respectively. Polarization studies showed that both the inhibitors under study were of mixed type. The results obtained by electrochemical impedance techniques were in good agreement with the results obtained by potentiodynamic polarization experiments. Some thermodynamic and activation parameters were computed based on the adsorption process. All the results confirmed that the inhibitive performance of MABIP was better than NABIP. The results obtained from

SEM, EDS, AFM and Langmuir adsorption isotherm confirmed that the mechanism of corrosion inhibition occurred through the adsorption process. Density functional theory was employed for theoretical calculations<sup>42</sup>.

**Valle-Quitana *et al.***, evaluated the corrosion inhibitory properties of phthalocyanine blue, an organic dye carried out in 0.5M sulfuric acid by using polarization curves, electrochemical impedance spectroscopy and gravimetric tests. Different dye concentrations (0, 100, 200, 400, 600, 800 ppm) were used and studies were carried out at temperature range from 25 - 60° C. The results indicated that phthalocyanine blue was a good corrosion inhibitor. At 25 and 40° C, Nyquist data displayed a single capacitive, depressed loop, indicating that the corrosion process was under charge transfer control, but at 60°C an inductive loop appeared indicating that the corrosion process is under adsorption/desorption control<sup>43</sup>.

**Elmsellem *et al.***, examined the inhibitive effect of pyrimidine derivatives namely N-((3,5-dimethyl-1H-pyrazol-1-)methyl)pyrimidin-2-amine (pym1), 2-((3,5-dimethyl-1H-pyrazol-1-yl)methyl)amino)pyrimidine-4,6-diol (pym 2) and 2-(((3,5-dimethyl-1H-pyrazol-1-yl)methyl)amino)-6-methylpyrimidine-4-ol (pym 3) on mild steel corrosion in 1M HCl. The results obtained from all the investigated compounds indicated that the inhibition efficiency was dependent on concentration and molecular structure. The inhibition efficiency followed the order pym 2 > pym 3 > pym 1. All the synthesized pyrimidine derivatives were found to be cathodic-type inhibitors. The effect of molecular structure on inhibition efficiency using DFT calculations has been discussed. The obtained results showed that the experimental studies and theoretical studies correlated well<sup>44</sup>.

**Sudheer *et al.***, synthesized and investigated three pyridine derivatives namely 2-amino-3,5-dicarbonitile-4-(4-methoxyphenyl)-6-(phenylthio)pyridine (ADTP I), 2-amino-3,5-dicarbonitile-4-phenyl-6-(phenylthio)pyridine (ADTP II), 2-amino-3,5-dicarbonitile-4-(4-nitrophenyl)-6-(phenylthio)pyridine (ADTP III) as corrosion inhibitors for mild steel in acid medium by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopic techniques. ADTP 1 showed highest inhibition efficiency of 97.6 % at 1.22 mmol L<sup>-1</sup>. At optimum concentration, the order of inhibition efficiencies for the pyridine derivatives were ADTP I > ADTP II > ADTP III. The

influence of temperature and their relative kinetic parameters were worked out. In order to inspect the surface modifications and composition of the inhibitor film, scanning electron microscope and energy dispersive X-ray spectroscopic studies were carried out<sup>45</sup>.

**Arukalam *et al.***, explored and studied the corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by hydroxy propylmethyl cellulose (HPMC). The studied inhibitor was investigated by weight loss and electrochemical techniques. The results obtained from the studied techniques showed that HPMC served as an effective inhibitor in both the acid medium. Inhibition efficiency of HPMC was enhanced by the addition of KI. The adsorption of HPMC was found to follow Langmuir isotherm and polarization studies clearly indicated that the studied inhibitor behaved as mixed-type. Quantum chemical calculations and molecular dynamic simulation were performed to explain the adsorption characteristics and configuration of HPMC at molecular level. The theoretical prediction showed good agreement with experimental findings<sup>46</sup>.

**Xavier *et al.***, studied the effect of substitution at 3 and 3, 5-positions of 2-6-diphenylpiperidin-4-one on mild steel corrosion in 1N H<sub>2</sub>SO<sub>4</sub> solution. Corrosion inhibition was evaluated by weight loss, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (Tafel) methods and their results were compared. The effect of anions (Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>) was studied by weight loss method and their synergism parameters were calculated. The adsorption of piperidine-4-ones obeyed Langmuir adsorption isotherm and involved both type of interactions (physical and chemical adsorption). The formation of protective film was supported by FTIR and SEM analysis<sup>47</sup>.

**Odozi *et al.***, investigated the use of 2,4-di-tert-butyl-6-(1h-phenantro[9,10-d]imidazol-2-yl) phenol (PIP) for corrosion of mild steel immersed in 0.5M H<sub>2</sub>SO<sub>4</sub> by weight loss and hydrogen evolution techniques at 303 – 333 K. PIP was found to be an effective corrosion inhibitor at all temperatures studied and performed better at 303 K. The inhibitive action of PIP in the acid solution was best described by Temkin adsorption isotherm. The Arrhenius and transition state equations were used to calculate the activation parameters and the mechanism of physical adsorption was proposed for PIP

from the obtained values of  $E_a$  and  $\Delta G_{ads}^0$ . PIP was recommended as green corrosion inhibitor for industries<sup>48</sup>.

**Ganesh.**, made an attempt to study the corrosion behaviour of Ethylene-1,1'-dimethyl-4,4'-bipyridinium iodide (Edpi) on mild steel corrosion in 0.5M sulfuric acid solution using electrochemical techniques such as potentiodynamic polarization and electrochemical impedance spectroscopy. The electrochemical investigations of Edpi were performed at different temperatures. The measurement of potentiodynamic polarization revealed that Edpi acted as mixed type inhibitor with predominant anodic effect. The adsorption process obeyed Langmuir adsorption isotherm<sup>49</sup>.

**Yildiz et al.**, investigated the corrosion inhibiting effect of 4,6-diamino-2-pyrimidinethiol (4D2P) on mild steel corrosion in 0.1M HCl using electrochemical techniques and theoretical calculations. The polarization studies showed that 4D2P acted as mixed type inhibitor but predominantly cathodic. SEM was used to analyse the surface adsorbed film. The adsorption of 4D2P on mild steel surface followed Langmuir model. To enhance the investigation of the electronic interaction between 4D2P molecules and the mild steel surface, several theoretical parameters were calculated which showed that the electron densities of both LUMO and HOMO were mainly localized over the entire compound<sup>50</sup>.

**Ezhilarasi et al.**, synthesized and investigated the corrosion inhibitory effects of 1-acetyl-4,5-dihydro-5-bromophenyl-3-(thiophen-2yl) pyrazoles on mild steel in 1M  $H_2SO_4$  and 1M HCl. Corrosion inhibition was evaluated by weight loss, potentiodynamic and electrochemical impedance studies. The synthesized inhibitor was characterized by FTIR,  $^1H$  NMR,  $^{13}C$  NMR and mass. The results indicated that corrosion inhibition performance of pyrazole was found to be good in both the acid medium. Synergistic effect of anions ( $Cl^-$  and  $I^-$ ) was studied by weight loss method. Tafel slopes obtained from polarization studies indicated that the inhibitor under study behaved as mixed type<sup>51</sup>.

**Ezhilarasi et al.**, studied the inhibitive effect of synthesized 1-acetyl-4,5-dihydro-5-phenyl-3-(thiophen-2yl) pyrazoles on mild steel in molar solution of  $H_2SO_4$  and HCl was studied by weight loss, potentiodynamic and electrochemical impedance studies. The results revealed that inhibition efficiency increased with increase in concentration of the



inhibitor and decreased with increase in temperature. The adsorption on mild steel surface obeyed Langmuir isotherm. Polarization studies showed that pyrazole compound acted as mixed type. Results obtained from weight loss, polarization curves and impedance spectroscopy were in good agreement<sup>52</sup>.

**Yadav *et al.***, studied the effect of synthesized spiropyrimidinethiones namely 6'-(4-methoxyphenyl)-1'-phenyl-2'-thioxo-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyrimidine]-2-one (MPTS) and 6'-(4-chlorophenyl)-1'-phenyl-2'-thioxo-2',3'-dihydro-1'H-spiro[indoline-3,4'-pyrimidine]-2-one (CPTS) on corrosion of mild steel in 15% HCl solution. The inhibitors were investigated by weight loss and electrochemical methods and quantum chemical calculations have been performed. Polarization studies indicated that MPTS and CPTS acted as mixed type but predominantly cathodic. The potential of zero charge ( $E_{PZC}$ ) for mild steel was also determined by electrochemical impedance spectroscopy. The protective nature of the adsorbed film on mild steel surface was confirmed by scanning electron microscopy, FT-IR, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy. The theoretical results obtained by density functional theory, were found to be consistent with the experimental results<sup>53</sup>.

## **2.2 Background to this work**

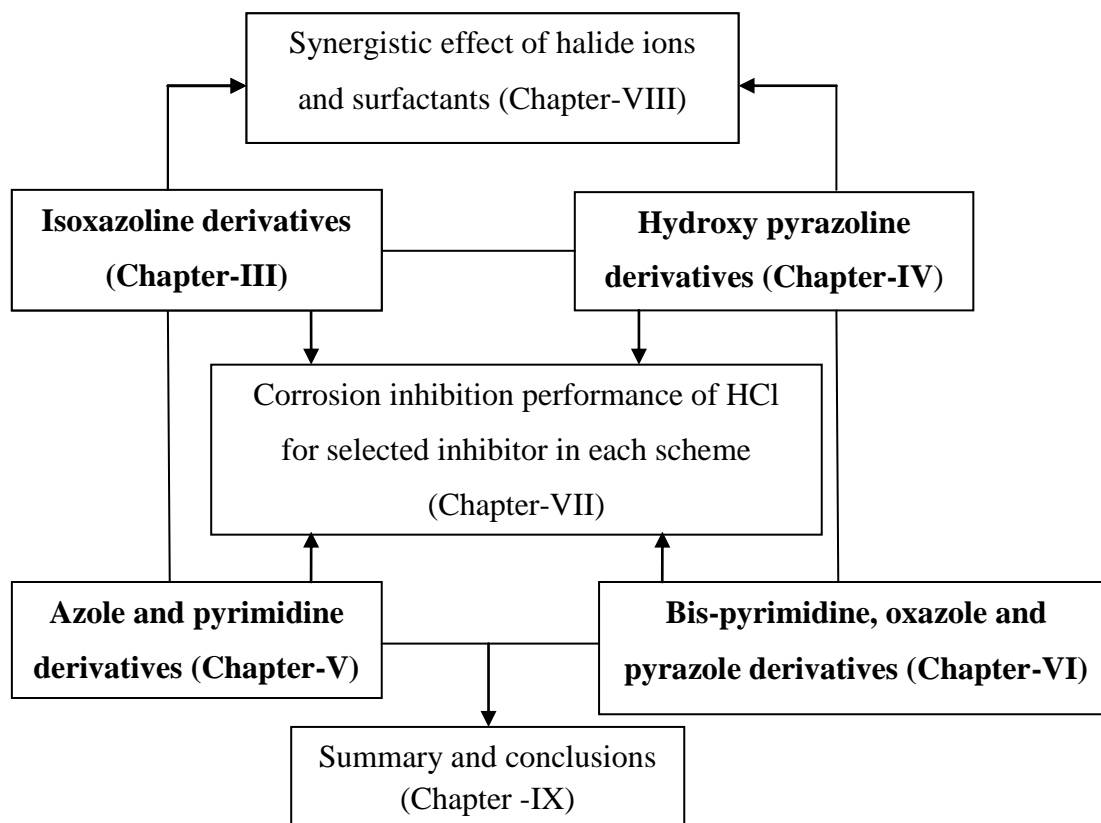
A perusal of literature reveals that less work has been carried out with azoles (isoxazolines and pyrazolines) and pyrimidine derivatives as corrosion inhibitors. Hence an attempt was made to synthesize these derivatives from chalcones and evaluate their corrosion inhibition properties. In order to support the experimental investigations some density functional theory (DFT) based quantum chemical calculations have been performed for the synthesized derivatives.

## **2.3 Objective to this work**

- To know the corrosion inhibition performance of isoxazolines, hydroxy pyrazolines, azoles, pyrimidines and its bis derivatives from chalcones.
- The synthesized heterocyclic compounds were characterized by FTIR spectra and apply these compounds for the corrosion protection of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> medium.

- To identify the optimal experimental condition for their maximum inhibition efficiency and to derive the adsorption kinetics from the weight loss data.
- The best inhibitors in each series were selected and their inhibition efficiency in 2M HCl was evaluated by electrochemical and non-electrochemical techniques.
- Synergistic effect of halide ions and surfactants on the corrosion inhibition efficiency of isoxazolines and hydroxy pyrazolines are performed.
- Surface analyses were also carried out to establish the mechanism of corrosion inhibition.
- Quantum chemical calculations have been performed using DFT in aqueous phase in both non-protonated and protonated form.

#### 2.4 An Overview of the objectives and aims of this thesis



## 2.5 REFERENCES

1. F. Bentiss, M. Lagrenee, J. Mater. Environ. Sci., **2** (2011) 13.
2. S.S. Abdel-Rehim, K.F. Khaled, N.A. Al-Mobarak, Arab. J. Chem., **4** (2011) 333.
3. N.O. Eddy, E.E. Ebenso, U.J. Ibok, E.E. Akpan, Int. J. Electrochem. Sci., **6** (2011) 4296.
4. S. Chitra, K. Parameswari, M. Vidhya, M. Kalishwari, A. Selvaraj, Int. J. Electrochem. Sci., **6** (2011) 4593.
5. N.F. Atta, A.M. Fekry, H.M. Hassaneen, Int. J. Hydrogen Energy., **36** (2011) 1.
6. K.F. Khaled, S.S. Abdel-Rehim, Arab. J. Chem., **4** (2011) 397.
7. A.Y. Musa, A.B. Mohamad, A.A.H. Kadhum, M.S. Takriff, Int. J. Electrochem. Sci., **6** (2011) 2758.
8. A.M. Fekry, M.A. Ameer, Int. J. Hydrogen Energy., **36** (2011) 11207.
9. A.K. Singh, S. K. Shukla, M.A. Quraishi, Int. J. Electrochem., **6** (2011) 5802.
10. A. Doner, R. Solmaz, M. Ozcan, G. Kardas, Corros Sci., **53** (2011) 2902.
11. N.O. Obi-Egbedi, I.B. Obot, Corros Sci., **53** (2011) 263.
12. F. Bentiss, B. Mernari, M. Traisnel, H. Vezin, M. Lagrenee, Corros Sci., **53** (2011) 487.
13. Y.S. Kara, S.G. Sagdinc, 25<sup>th</sup> National chemistry congress with international participation., (2011) 256.
14. S.K. Shukla, A.K. Singh, M.A. Quaraishi, Int. J. Electrochem. Sci., **7** (2012) 3371.
15. R.S. Abdel Hameed, H.I. Al-shafey, A.S. Abul Magd, H.A. Shehata, J. Mater. Environ., **3** (2012) 294.
16. K. Aderdour, R. Tourir, M. Ebn Touhami, M. Sfaira, H.El. Kafssaoui, B. Hammouti, H. Benzaid, El M. Essarsi, Der Pharma Chemica., **4** (2012) 1485.
17. M.P. Chakaravarthy, K.N. Mohana, Int. J. Corros., (2012) 1.
18. R. Tripathi, A. Chaturvedi, R.K. Upadhayay, Res. J. Chem. Sci., **2** (2012) 18.
19. I.B. Obot, E.E. Ebenso, I.A. Akpan, Z.M. Gasem, Ayo S. Afolabi, Int. J. Electrochem. Sci., **7** (2012) 1978.
20. M.M. Kabanda, L.C. Murulana, M. Ozcan, F. Karadag, I. Dehri, I.B. Obot, E.E. Ebenso, Int. J. Electrochem. Sci., **7** (2012) 5035.
21. S. Harikumar, S. Karthikeyan, J. Mater. Environ. Sci., **4** (2013) 675.

22. X. Wang, Y. Wan, Q. Wang, F. Shi, Z. Fan, Y. Chen, *Int. J. Electrochem. Sci.*, **8** (2013) 2182.
23. S. Manimegalai, R. Ramesh, P. Manjula, *Res. Desk.*, **2** (2013) 326.
24. X. Wang, Y. Wan, Q. Wang, Y. Ma, *Int. J. Electrochem. Sci.*, **8** (2013) 806.
25. A.S. Fouda, A.M. Eldesoky, M.A. Elmorsi, T.A. Fayed, M.F. Atia, *Int. J. Electrochem. Sci.*, **8** (2013) 10219.
26. Y.S. Kara, S.G. Sagdinc, *Asian J. Chem.*, **25** (2013) 7904.
27. A. Ghazoui, N. Bencat, S.S. Al-Deyab, A. Zarrouk, B. Hammouti, M. Ramdani and M. Guenbour, *Int. J. Electrochem. Sci.*, **8** (2013) 2272.
28. I. El Ouali, A. Chetouani, B. Hammouti, A. Aouniti, R. Touzani, S.El Kadiri and S. Nlate, *Electrochim. Acta.*, **31** (2013) 53.
29. M. Scendo, J. Trela, *Int. J. Electrochem. Sci.*, **8** (2013) 8329.
30. S. Junaedi, A.A. Al-Amiery, A. Kadhum, A.A.H. Kadhum, A.B. Mohamad, *Int J Mol Sci.*, **14** (2013) 11915.
31. N.O. Obi-Egbedi, I.B.Obot, *Arab. J. Chem.*, **6** (2013) 211.
32. M. Yadav, D. Behera, S. Kumar, R. Ranjan Sinha, *Ind. Eng. Chem.*, **52** (2013) 6318.
33. M. Jannathul Firdhouse, D.Nalini, *J. Chem.*, Doi; 10.1155/2013/835365.
34. R. Tourir, R.A. Belakhmima, M. Ebn Touhami, L. Lakhrissi, M.El. Fayed, B. Lakhrissi, E.M. Essassi, *J. Mater. Environ. Sci.*, **4** (2013) 921.
35. S. Ananth Kumara, Dr. A. Sankar, A.S. Rameshkumar, *Am. J. Engg.Res.*, **2** (2013) 17.
36. P. Udhayakala, A. Maxwell Samuel, T.V. Rajendiran, S. Gunasekaran, *Der Pharma Chemica.*, **5** (2013) 111.
37. A. Ousslim, A.Chetouani, B. Hammouti, K. Bekkouch, S.S. Al-Deyab, A. Aouniti, A. Elidrissi, *Int. J. Electrochem. Sci.*, **8** (2013) 5980.
38. P. Mourya, S. Banerjee, R. Bala Rastogi, M. Mohan Singh, *Ind. Eng. Chem. Res.*, **52** (2013) 12733.
39. A.A. Al-Amiery, A.A.H. Kadhum, A. Kadhum, A.B. Mohamed, C.K. How, S. Junedi, *Mater.*, **7** (2014) 787.
40. H. Ju, L. Ding, C. Sun, Jie-jing Chen, *Adv. Mat. Sci. Engg.*, Doi; 10.1155/2014/519606.

41. D.M. Gurudatt, K.N. Mohana, *Ind. Eng. Chem. Res.*, **53** (2014) 2092.
42. M. Yadav, S. Kumar, I. Bahadur, D. Ramjugernath, *Int. J. Electrochem. Sci.*, **9** (2014) 3928.
43. J.C. Valle-Quitana, G.F. Dominguez-Patino, J.G. Gonzalez-Rodriguez, *Int. J. Corros.*, Article ID 945645 (2014)
44. H. Elmsellem, A. Aouniti, M. Khoutoui, A. Chetouani, B. Hammouti, N. Benchat, R. Touzani, M. Elazzouzi, *J. Chem. Pharm. Res.*, **6** (2014) 1216.
45. S. Sudheer, M.A. Quraishi, *Ind. Eng. Chem. Res.*, **53** (2014) 2851.
46. I.O. Arukalam, I.O. Madu, N.T. Ijomah, C.M. Ewulonu, G.N. Oneyeagoro, *J. Mat.*, Doi; 10.1155/2014/101709.
47. G.T. Xavier, B. Thirumalairaj, M. Jaganathan, *Int. J. Corros.*, Doi; 10.1155/2015/410120.
48. N.W. Odozi, J.O. Babalola, E. B. Ituen, A. O. Eseola, **4** (2015) 1-9.
49. A. Ganash, *Int. J. Electrochem. Sci.*, **10** (2015) 4439.
50. R. Yildiz, *Corros. Sci.*, **90** (2015) 544.
51. M.R. Ezhilarasi, B. Prabha, T. Santhi, *Rasayan J. Chem.*, **8** (2015) 71.
52. M.R. Ezhilarasi, B. Prabha, T. Santhi, *Chem. Sci. Trans.*, **4** (2015) 758.
53. M. Yadav, R.R. Sinha, Sumit Kumar, T.K. Sarkar, *Rsv. Adv.*, Doi; 10.1039/C5RA14406J (2015).