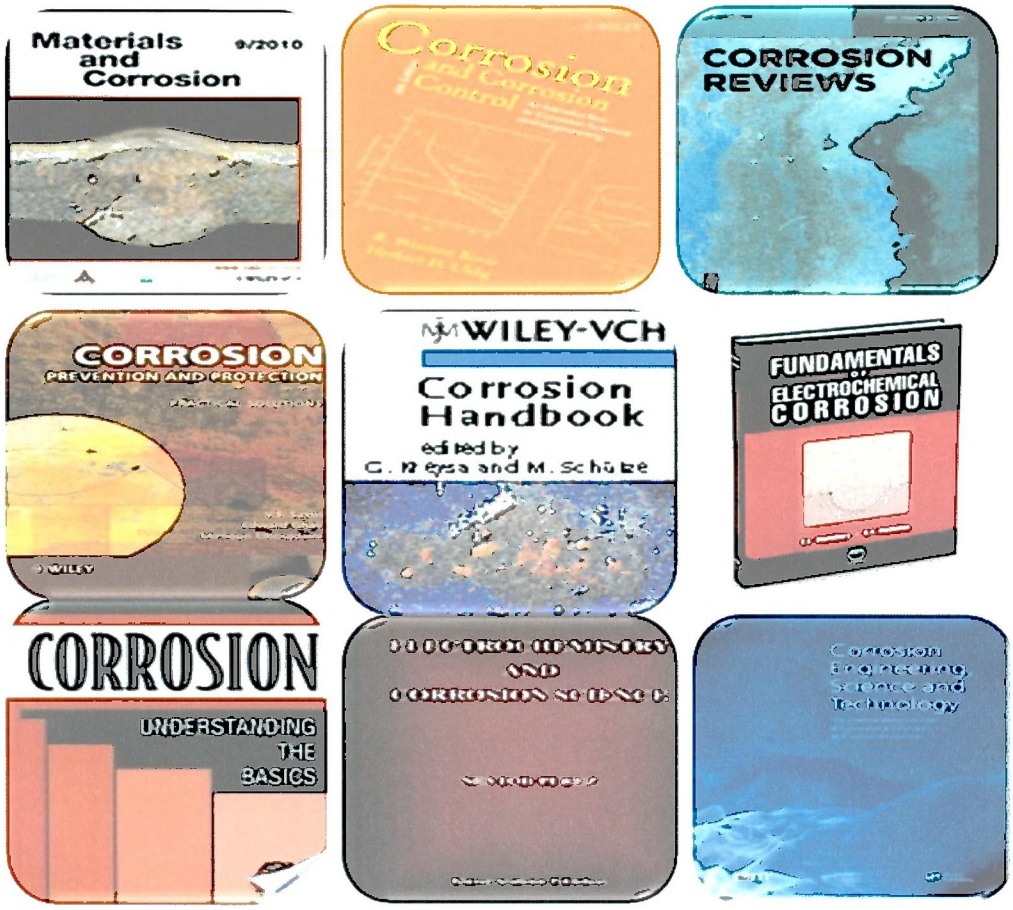

REVIEW OF LITERATURE

CHAPTER II
REVIEW OF LITERATURE

An acquaintance with related literature of past studies is a must for any research for formulating sound methodology which acts as a persevering force during the outset of research. From this literature, new areas of research can be inferred.

The present investigation on **"Adsorption Behaviour and Corrosion Inhibitive Potential of Imidazoline Derivatives on Mild Steel/Acid Interface"** is reviewed under the following topics:

- Organic compounds as corrosion inhibitors
- Synergistic effect
- Effect of Concentration, Time and Temperature
- Adsorption Isotherm
- Kinetic and Thermodynamic parameters
- Mode of action & Mechanism
- Electrochemical parameters
- Nitrogen containing compounds
- Imidazoline derivatives as corrosion inhibitors
- Quantum Chemical Studies.

Corrosion problems have received a considerable amount of attention because of their attack on materials. The use of inhibitors is one of the most practical methods for protection against corrosion. Several researchers have studied the influence of organic compounds containing nitrogen on the corrosion of steel in acidic media, most organic inhibitors act by adsorption on the metal surface **(Sanyal 1981, Abd El–Maksoud 2008)**

2.1 Organic compounds as corrosion inhibitors

Most organic inhibitors contain at least one polar group with an atom of nitrogen, sulphur or in some cases selenium and phosphorus. According to **Hackerman *et al.*, (1965)** the inhibiting properties of many compounds were determined by the electron density at the reaction center. With an increase in the electron density at the reaction center, the chemisorption bonds between the inhibitor and the metal are strengthened.

Hackerman *et al.*, (1951) investigated the adsorption of organic substances with a long hydrocarbon chain from organic solvents. These studies showed that the better the substance is adsorbed, the more effectively it protects the surface

The mode of corrosion inhibition of pure iron due to phenyl-5-mercapto-1,2,3,4-tetrazole (PMT) in molar HCl was studied through weight loss and electrochemical steady-state experiments. The action of corrosion inhibition due to PMT was compared with the action of other organic compounds of the same family such as 1,2,3,4-tetrazole (TTZ) and 1-methyl-5-mercapto-1,2,3,4-tetrazole (MMT). PMT was found to be a more efficient corrosion inhibitor than the other tetrazole compounds studied because of its sulphur atom, four nitrogen atom and aromatic centre **(Kertit *et al.*,1996)**.

Gamal.K.Gomma *et al.*, (1998) evaluated the corrosion of low-carbon steel in sulphuric acid in the presence of pyrazole-halide mixture by weight loss and polarization techniques at various temperatures. The surface coverage values θ increased in the order I>Br>Cl indicating that the radii and the electronegativity of halides play an important role in the process of adsorption.

The effect of changing functional groups of some amides and thiosemicarbazone derivatives on their inhibition efficiency had been reported with a view to establish a relationship between inhibitor efficiency and molecular structure, using weight loss and hydrogen evolution techniques. The compounds used for this study are urea (U), thiourea (TU), acetamide (A), thioacetamide (TA), semicarbazide (SC), thiosemicarbazide (TSC), methoxybenzaldehyde thiosemicarbazone (MBTSC), 2-acetylpyridine-(4-phenyl) thiosemicarbazone (2AP4PTSC), 2- acetylpyridine-(4-methyl) thiosemicarbazone (2AP4MTSC), benzoin thiosemicarbazone (BZOTSC) and benzil thiosemicarbazone (BZITSC). All the compounds inhibited corrosion to varying degrees. It was found that the molecules which include a thiocarbonyl group, e.g. TU, TA and TSC, have higher inhibition efficiency than the corresponding compounds which do not, e.g. U, A and SC. The results (at 30°C and 40°C) indicate that the order of efficiency of the thiocompounds in solution and the extent of their tendency to adsorb on mild steel surfaces were as follows: TSC > TU > TA, whereas for the thiosemicarbazone derivatives, the order was BZOTSC > BZITSC > MBTSC > 2AP4MTSC < 2AP4PTSC. Physical adsorption mechanism have been proposed for

all the inhibitors except MBTSC, BZITSC and BZOTSC, which are chemically adsorbed **(Abd El *et al.*, 2008).**

The corrosion inhibition behaviour of some substituted dithiobiurets, namely, -1,5-diphenyl-2,4-dithiobiuret (DPDTB), 1-tolyl-5-phenyl-2,4-dithiobiuret (TPDTB), 1-anisidyl-5-phenyl-2,4-dithiobiuret (APDTB), 1-chorophe- nyl-5-diphenyl-2,4-dithiobiuret (CPDTB) were studied in 1 to 5 M HCl on mild steel. The characteristics of these compounds were explained in terms of factors such as inhibitor concentration, acid concentration, temperature, immersion time and molecular structure. Potentiodynamic polarization and A.C impedance techniques were used to investigate the inhibition mechanism. Among the compounds studied APDTB exhibited the best performance giving more than 98% inhibition efficiency (IE) in HCl solutions. DPDTB and CPDTB were found to reduce hydrogen permeation through mild steel in HCl solutions. The adsorption of APDTB was also confirmed by Auger electron spectroscopy (AES) **(Quraishi *et al.*, 2000).**

The corrosion inhibition characteristics of 2-amino thiophenol (ATP) and 2-cyanomethyl benzothiazole (CNMBT) on two types of steel in 1 M HCl medium were investigated at different temperatures (25, 30, 35, 40 and 50°C). The effects of the inhibitors on the general corrosion of the two samples were investigated by using gravimetric and galvanostatic polarization techniques. The inhibition efficiencies increased with increase in the concentration but decreased with increase in temperature. The inhibition efficiency of CNMBT was found to be higher than that of ATP **(Abd El *et al.*, 2008).**

The efficiency of 2,5-bis(n-methoxyphenyl)-1,3,4-oxadiazoles (n-MOX), as corrosion inhibitors for mild steel in 1 M HCl and 0.5 M H_2SO_4 was determined by weight loss measurements and electrochemical studies. The results showed that these compounds acted as good corrosion inhibitors even at very low concentrations. Comparison of results among those obtained by the studied oxadiazoles showed that 2-MOX was the best inhibitor. The adsorption of 2-MOX on the mild steel surface in both acidic media followed a Langmuir isotherm model. Significant correlations were obtained between inhibition efficiency with the calculated chemical indexes, indicating that variation of inhibition with structure of the inhibitors may be explained in terms of electronic properties **(Bentiss *et al.*, 2002).**

The effect of thiourea (TU), methyl thiourea (MTU) and phenyl thiourea (PTU) on the corrosion behaviour of mild steel in 0.1M solution of H_2SO_4 was investigated using electrochemical studies. The experimental results revealed that phenyl thiourea was the most efficient and thiourea the least. Replacement of hydrogen atom of amino group of thiourea molecule by methyl and phenyl groups caused the increase in percentage of inhibition efficiencies **(Ozcan *et al.*, 2004).**

The influence of derivatives of 1,2,4-triazole, 3-amino-1,2,4-triazole (ATA), 3-amino-5-mercapto-1,2,4 triazole (AMT) and 3-amino-5-methylthio-1,2,4 triazole (AMTT) and ionic surfactants cetyl trimethyl ammonium bromide (CTAB) and sodium dodecyl sulphate (SDS) on the corrosion control of copper in acidic solution was investigated by gravimetric and electrochemical methods. AMTT was found to be a more powerful corrosion inhibitor than ATA and AMT. The higher inhibition efficiency observed with AMTT containing both nitrogen and sulphur atoms might be attributed to the presence of more number of lone pair of electrons and the presence of electron releasing methyl groups **(Lalitha *et al.*, 2005)**.

Several new isoxazolidines having varying degree of steric environment and hydrophobic chain length, prepared efficiently using single-step nitrone cycloaddition reactions, were tested for corrosion inhibition of mild steel in 1M and 5M HCl at 50-70^{o}C range by gravimetric and electrochemical methods. All compounds exhibited very good corrosion inhibition efficiency in acidic solution **(Abd El *et al.*, 2008).**

Corrosion inhibition of mild steel in 0.5 M H_2SO_4 in the temperature range 30–60^{0}C using sodium naphthalene disulphonic acid (NDSA) as an inhibitor was studied. The inhibition efficiency increased with the increase in concentration of NDSA till a critical value which is independent on temperature. The adsorption of inhibitor at 30^{o}C followed Flory–Huggins adsorption isotherm **(Abd El *et al.*, 2008).**

Novel corrosion inhibitors, namely 1-{2-[(2-hydroxyethyl) thio] ethyl} pyrrolidin-2-one (P5) and {[2-(2-oxopyrrolidin-1-yl) ethyl] thio} acetic acid (P4), were synthesized and tested as corrosion inhibitors for steel in 0.5 M H_2SO_4. The effects of P4 and P5 were also compared to their initial reactants 1-vinylpyrrolidin-2-one (P1), 2-mercaptoethanol (P2) and mercaptoacetic acid (P3). The study was carried out by weight loss measurements, potentiodynamic polarisation, linear polarization resistance (R_p) and electrochemical impedance spectroscopy (EIS) methods. The inhibition efficiency increased with the concentration of P5 to attain 89% at 5 x 10^{-3}

M. Polarisation measurements showed that the pyrrolidones act essentially as cathodic inhibitors **(Bouklah *et al*., 2006).**

Bentiss *et al.*, (2007) examined the inhibition efficiencies of the different 4*H*-triazole derivatives, namely 3,5-diphenyl-4*H*-1,2,4-triazole (DHT), 3,5-bis(4-pyridyl)-4*H*-1,2,4-triazole(4-PHT) and 3,5-bis(4-methylthiophenyl)-4*H*-1,2,4-triazole(4MTHT) for corrosion and dissolution protection of mild steel in normal hydrochloric acid solution using weight loss and electrochemical techniuques. The better performance of MTHT (IE- 99.6%) compared to DHT, PHT was due to the electron releasing group – SCH_3, giving a favourable electron density for adsorption interactions.

Benzotriazole derivatives, namely, N-[1-(benzotriazolo-1-yl)alkyl] aryl amine (BTMA), N-[1-(benzotriazolo-1-yl)aryl] aryl amine (BTBA), and 1-hydroxy methyl benzotriazole (HBTA), were synthesized and their inhibition behaviour on mild steel in 0.5M H_2SO_4 at room temperature was investigated by various techniques. Potentiodynamic polarization and AC impedance studies were used to investigate the inhibitor mechanism. Benzotriazole derivatives were found to act as mixed type inhibitors. Among the compounds studied, HBTA exhibited the best performance giving more than 95% IE in H_2SO_4 solutions.

The corrosion studies of mild steel/1-methyl-4[4'(-X)-styryl] pyridinium iodides (X: -H, $-CH_3$ and $-OCH_3$)/hydrochloric acid systems was studied at different temperatures by means of hydrogen evolution and weight loss measurements. Results show that with increasing the donor property of the substituent, the inhibition efficiency of the inhibitor increased in the order: I-H<II-CH_3<III-OCH_3 **(Etheram Noor *et al.*, 2008)**.

2,5-bis(4-dimethylaminophenyl)-1,3,4-thiadiazole (DAPT) was synthesized and its inhibiting action on the corrosion of mild steel in 1 M HCl and 0.5 M H_2SO_4 at 30°C was investigated by various corrosion monitoring techniques. At constant acid concentration, inhibition efficiency increased with concentration of DAPT and was found to be more efficient in 0.5 M H_2SO_4 than in 1 M HCl. Potentiostatic polarization studies showed that DAPT was a mixed-type inhibitor. The effect of temperature on the corrosion behaviour of mild steel in 1 M HCl with addition of DAPT was studied in the temperature range from 25 to 60°C. It was shown that adsorption was consistent with the Langmuir isotherm for 30°C. **(Abd .El. Maksoud *et al.*, 2008).**

2.2 Synergistic effect

Synergism is a combined action of compounds greater in total effect than the sum of the individual effects. Synergism of corrosion inhibitors may be due to the interaction between components of the inhibitor composition or due to interaction between the inhibitor and one of the ions present in the aqueous solution. On addition of halide salt to acid solution containing any organic compound, a co-operative effect results which inhibits iron corrosion. Halides have been reported to inhibit the corrosion of some metals in strong acids and this effect depends on the ionic size and charge, the electrostatic field set up by the negative charge of the anion on adorption sites and the nature and concentration of halide ions. In acid solutions, halides are known both to stimulate and inhibit the corrosion of metals. Halide ions are found to enhance the inhibitive effect of several nitrogen containing compounds of mild steel in acidic solutions.

The inhibition behaviour of 3,5-bis(4-methylthiophenyl)-4H-1,2,4-triazole (4-MHT) and its synergistic effect with KI for mild steel in 0.5 M H_2SO_4 was investigated using weight loss measurements and different electrochemical techniques such as potentiostatic polarization curves and electrochemical impedance spectroscopy (EIS). The addition of Potassium iodide (KI) enhanced the inhibition efficiency considerably. A synergistic effect was observed between KI and 4-MTHT with an optimum mass ratio of [4-MTHT]/[KI]= $4x10^{-2}$. The synergism parameters calculated from surface coverage were found to be more than unity. This result clearly showed the synergistic influence of iodide ions on the corrosion inhibition of mild steel in 0.5 M H_2SO_4 by 4-MTHT. The adsorption of this inhibitor alone and in combination with iodide ions followed Langmuir adsorption isotherm. **(Abd *et al.*, 2008).**

Corrosion inhibition of mild steel in 2 M HCl and 1 M H_2SO_4 by leaf extracts of *Occimum viridis* (OV) was studied using the gasometric technique at temperatures of 30 and 60 °C. The results indicate that the extracts inhibit the corrosion process in both acid media and inhibition efficiency increased with concentration. Synergistic effects increased the inhibition efficiency in the presence of halide additives namely KCl, KBr, KI. Comparative analysis of the inhibitor adsorption behaviour in 2 M HCl and 1 M H_2SO_4 as well as the effect of halide additives suggest that cationic species

may not be the only constituents responsible for the inhibiting action of the extract. **(Emeka.E.Oguzie *et al.*, 2006).**

The corrosion inhibition of cold rolled steel in 0.5 M H_2SO_4 in the presence of o-phenanthroline and sodium chloride was investigated by using weight loss and electrochemical techniques. The experimental data suggest that the inhibition efficiency increased with increasing NaCl concentration in the presence of 0.0002 M o-phenanthroline, but decreased with increasing temperature. Synergistic effect was observed when o-phenanthroline and chloride ions were used together to prevent cold rolled steel corrosion in 0.5 M H_2SO_4. The experimental results suggested that the presence of chloride ions in the solution stabilized the adsorption of o-phenanthroline molecules on the metal surface and improved the inhibition efficiency of o-phenanthroline. **(Abd *et al.*, 2008).**

A macrocyclic compound, namely 2,3,9,10-tetraphenyl-6,13-dithia-1,4, 5, 7, 8,11,12,14-octaaza-cyclotetradeca-1,3,6,8,10,13-hexaene (PTAT) was synthesized to study the corrosion inhibitive effect on pickling of mild steel in 20% H_2SO_4 at 95°C. The synergistic effect of this compound was studied by weight-loss, potentiodynamic polarization, electrochemical impedance spectroscopy and hydrogen permeation studies. The results of this investigation revealed an enhancement in inhibition efficiency (IE) for 500 ppm PTAT in the presence of 0.25% KI as a synergist. **(Abd *et al.*, 2008).**

The inhibitive effect of congo red dye (CR) on mild steel corrosion in sulphuric acid solution was studied at different temperatures using gravimetric techniques. The influence of halide additives namely: KCl, KBr and KI on the inhibition efficiency of CR were also investigated. Inhibition efficiency increased with CR concentration but decreased with rise in temperature.Inhibition antagonism and synergism were respectively observed at 30 and 60°C on addition of halide salts to inhibited systems containing CR. The calculated values of heat of adsorption confirmed physisorption and chemisorption mechanisms respectively for CR adsorption in the absence and presence of halides. **(Abd *et al.*, 2008).**

2.3 Effect of Concentration, Time and Temperature

The inhibitive performance of 4-amino-3-butyl -5- mercapto-1,2,4-triazole (ABMT) on the corrosion of mild steel in 1N sulphuric acid was investigated by weight loss and polarization techniques. The inhibition efficiency increased with

increase in concentration and temperature, indicating that the inhibitor film formed on the metal surface was protective in nature at higher temperature. Adsorption of the inhibitor on mild steel obeyed Temkin adsorption isotherm and the investigated inhibitor is of mixed type **(Quraishi *et al.*, 2002)**.

Oxadiazole derivatives were investigated as corrosion inhibitors for mild steel in sulphuric acid by **Boukhal *et al.*, (2006)** using weight loss method at temperature ranges (303K to 343K). The oxadiazoles performed excellently as effective inhibitors and obeyed Langmuir adsorption.

Diethyl pyrazine-2,3-dicarbozylate (Prz) was evaluated as a corrosion inhibitor for steel in sulphuric acid solution using electrochemical impedance spectroscopic technique. The results obtained showed that Prz acted as a good inhibitor. Prz was adsorbed on the steel surface according to Langmuir isotherm adsorption model. **(Kissi *et al.*, 2006).**

The inhibition efficiency of sparfloxacin for the mild steel in HCl was investigated by **Eddy *et.al.*, 2008** using gravimetric and thermometric methods. The efficiency increased with increase in concentration but decreased with increase in temperature. The adsorption of sparfloxacin was exothermic in nature**.**

A study on the effectiveness of Benzotriazole as a corrosion inhibitor for mild steel in 1M acetic acid was carried out by weight loss method. The result showed that the inhibition efficiency increased with increased in concentration of the inhibitor and the kinetic treatment of the results reveal first order kinetics **(Matheswaran *et al.*, 2010)**.

2.4 Adsorption isotherm

1) Adsorption isotherms are very important in determining the mechanism of organic electrochemical reactions. The adsorbability of stable organic compounds determines their inhibitive efficiency.

Thiazole derivatives proved to be effective inhibitors for corrosion of mild steel in hydrochloric acid. The various techniques used to study the influence were weight loss and potentiodynamic polarization studies. The thiazole derivatives obeyed Temkin adsorption isotherm and were mixed type inhibitors **(Quraishi *et al.*, 1996)**.

Abd El Rehim *et al.*, (1999) tested 4-amino antipyrine as a corrosion inhibitor for mild steel by weight loss, potentiodynamic polarization and Electrochemical impedance spectroscopy in 1M HCl. The inhibition efficiency increased with

increasing concentration but decreased with increasing temperature. The adsorption of the inhibitor followed Flory-Huggins isotherm. The inhibition was due to the adsorption of the inhibitor molecules on the steel surface and blocking of active sites.

Weight loss measurements, potentiostatic and potentiodynamic polarization studies were used to study the inhibitive action of the extract of *Ficus nitida* leaves towards general and pitting corrosion of C-steel, Ni and Zn. It was found that the presence of ficus extract in the corrosive media decreased the corrosion rate and the adsorption followed Langmuir adsorption isotherm **(El Etre *et al.*, 2006).**

The inhibitive effect of 6-benzyl amino purine (BAP) on the corrosion of cold rolled sheet (CRS) in H_2SO_4 was studied by weight loss and potentiodynamic polarization studies. FTIR and AFM were used to characterize the CRS surface. The adsorption of BAP obeyed the Temkin adsorption isotherm and acted as mixed-type inhibitor **(Xianghong *et al.*, 2009)**.

2[2-oxo-phenyl hydrazinyl ether]benzamide (2BA) was synthesized, characterized and tested as effective for corrosion inhibition of mild steel in 1N H_2SO_4 solution using galvanodynamic polarization, EIS techniques and surface morphology of the mild steel samples were analysed by SEM. Adsorption of 2BA followed Langmuir isotherm model. Polarization measurements show that 2BA acted as a mixed type inhibitor **(Rinki *et al.*, 2010)**.

The investigation of amino organic compounds as corrosion inhibitors for mild steel in 1M HCl by electrochemical measurement methods reveal that they obeyed Langmuir adsorption isotherm. **(Musa *et al.*, 2010).**

The effectiveness of Nizoral (NZR) as a corrosion inhibitor for mild steel in 0.1M H_2SO_4 was measured by weight loss method in the temperature range 30-50°C. The adsorption of the inhibitor was found to obey Langmuir and El Awady *et al* models. **(Ime Obot 2009).**

2.5 Kinetic and thermodynamic parameters

Thermodynamic adsorption parameters and kinetic corrosion parameters are a useful tool for clarifying the adsorption behaviour of an inhibitor.The well known thermodynamic parameters are the free energy of adsorption (ΔG_{ads}), the heat of adsorption (ΔH_{ads}) and the entropy of adsorption (ΔS_{ads}). In order to obtain more details on the corrosion process, activation energy kinetic parameters such as energy, enthalpy and entropy are evaluated from the effect of temperature.

Etheram Noor (2007) studied the temperature effect on mild steel corrosion in 2.0M HCl and H_2SO_4 in the absence and presence of aqueous extract of fenugreek leaves (AEFL). Thermodynamic data for both inhibitors led to suggest the occurrence of comprehensive adsorption for the inhibitor species on mild steel in HCl solution and chemical adsorption for H_2SO_4 solution.

The corrosion and inhibitor adsorption processes in mild steel/1-methyl-4[4'(-X)-styryl]pyridinium iodides (x: -H, $-CH_3$ and $-OCH_3$)/hydrochoric systems was carried out at different temperatures (25-60°C) by means of hydrogen evolution and weight loss measurements. On the basis of the kinetic and thermodynamic parameters a comprehensive adsorption was suggested **(Eheram Noor *et al*., 2008).**

The adsorption and inhibition effect of xanthione (XION) on mild steel in 0.5M H_2SO_4 at 303-333K were studied using gravimetric and UV-Vis spectrophotometric methods.The adsorption process was spontaneous, exothermic and accompanied with a decrease in entropy of the system from thermodynamic point of view.(**Obi-Egbedi *et al* .,2010)**

Obi-Egbedi *et al.*, (2010) studied the inhibition of Xanthene (XEN) on the corrosion of mild steel in 0.5M H_2SO_4 at 303-333K using gravimetric and UV-Vis spectrophotometric methods. Results of kinetic and thermodynamic parameters revealed physical adsorption mechanism; the process was spontaneous and zero-order kinetics with respect to the mild steel.

Weight loss measurements and potentiostatic polarization studies reveal that 2-hydrazine-6-methyl-benzothiazole (HMBT) acted as an effective inhibitor for the corrosion of mild steel in 1N HCl and 1N H_2SO_4. The inhibitor behaved predominantly as cathodic inhibitor in HCl and mixed type inhibitor in H_2SO_4 and was found to obey Langmiur adsorption isotherm in both the acid media **(Ajmal *et al.*, 1994)**.

New and effective aldimine as corrosion inhibitors for mild steel in HCl was reported by **Subramania. *et al.*, (2004)**. The adsorption of these compounds obeyed Temkin adsorption isotherm.

2.6 Mode of inhibition & mechanism

Corrosion inhibition of mild steel by Phenacyl dimehtyl sulfonium bromide and six of its p-substituted derivatives in 0.67M H_3PO_4 was studied using chemical,

electrochemical and SEM. The adsorption center was suggested to be the π-electrons of the phenyl ring **(Arab *et al.*, 2006)**.

Behpour *et al.*, (2009) stated that the effectiveness of Schiff bases of 2-{-1-methyl -3-[(sulfanyl phenyl)imino]butlylidene}-amino)-1-benzenethiol and 2-{-1-methyl -3-[(sulfanyl phenyl)imino]ehtylidene}-amino)-1-benzenethiol as corrosion inhibitors in acid solution for mild steel in acid solution may be due to the adsorption of the inhibitor on the metal surface by formation of a bond between the hetero atom pair of the inhibitor and /or the π-electron cloud of the metal.

The inhibition of mild steel corrosion in acidic medium by 1-methyl-3-pyridin-2-yl-thiourea may be due to the possible overlap of the π-electron system of the inhibitor with the vacant d-orbitals of the iron atom on the metal surface resulting in strong dπ- pπ interaction **(Hosseini & Azimi, 2009)**

A heterocyclic Schiff base furion thiosemicarbazone(FTSC) was tested for its corrosion inhibition towards mild steel in 1M HCl using weight loss, and electrochemical impedance spectroscopy. The high inhibition efficiency of the Schiff base towards mild steel may be due to the presence of azomethine C=N, N,O and S atoms in FTSC molecule **(Stanly Jacob *et al.*, 2010)**.

Oleo-chemicals triazole as effective corrosion inhibitors for mild steel in acetic acid media was investigated by **Ansari and Quraishi (2010)** using weight loss and potentiodynamic polarization techniques. The adsorption was found to occur through π-electron of aromatic ring and lone pair of electrons of nitrogen and sulphur atoms.

Hexamethylene diamine tetra methyl-phosphonic acid showed excellent inhibition properties for the corrosion of carbon steel in 0.5M HCl. The inhibitor adsorbed via donor-acceptor interactions between the unshared electron pairs of the heteroatams(P,N,O) form a bond with the vacant d orbitals of the iron atom on the metal surface, which act as a Lewis acid, leading to the formation of a protective chemisorbed film **(Laamari *et al.*, 2010)**.

2.7 Electrochemical parameters

The inhibitive effect of triazole derivative on the corrosion activity of mild steel in acid media was investigated using Tafel polarization technique, AC impedance measurements and continous linear polarization resistance method. The triazole derivative acted as a mixed inhibitor with a significant shift in the cathodic

direction. The corrosion rate was reduced by 95% for 50 ppm of the compound. **(Abdennabi *et al.*, 1996).**

The corrosion inhibition behaviour of some substituted dithiobiurets was studied in 1M to 5M HCl using weight loss, potentiodynamic polarization and AC impedance techniques. Potentiodynamic polarization studies reveal that the inhibitors behaved as mixed type inhibitors **(Quraishi *et al.*, 2000)**.

Weight loss and various electrochemical techniques were employed to study the inhibition action of 3,6-bis(2-methoxy phenyl)-1,2-dihydro-1,2,4,5-tetrazine on the corrosion of mild steel in acid media. Results obtained revealed that this organic compound performed as a very good inhibitor. The inhibitor behaved as a mixed type in 1M HCl and cathodic type in 0.5M H_2SO_4 solution **(Elkadi *et al.*, 2000)**.

Polarisation and AC impedance studies were carried out on the inhibition of carbon steel in 0.1M HCl solution by various Schiff bases containing hetero atomic substituents by **Yurt *et al.*, (2004)**. Schiff bases under investigation acted as an anodic inhibitor.

The inhibitive nature of Tween-40 on the corrosion of cold rolled steel in sulphuric acid was evaluated by weight loss and potentiodynamic polarization methods. Polarization curves show that tween-40 was reported as a cathodic – type inhibitor in Sulphuric acid **(Xianghong *et al.*, 2005)**.

Polydendate Schiff base compounds were synthesized and its corrosion behaviour of steel in 2M HCl were investigated by **Kaan *et al.*, (2006)** using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy. All the Schiff bases proved to be effective inhibitors. They acted as mixed type inhibitor.

2,2'- Dithio bis (3-cyano-4,6-dimehtylpydridine) was synthesized and its inhibiting action on the corrosion of mild steel in H_2SO_4 was investigated by polarisation curves and Electrochemical impedance spectroscopy. EIS showed that the charge transfer controlled the corrosion process in the uninhibited and inhibited solutions and it acted as mixed type inhibitor **(Morad *et al.*, 2006)**.

The inhibition effect of some fatty acid oxadiazoles for corrosion inhibition of mild steel in HCl was carried out by weight loss, potentiodynamic polarization technique, electrochemical impedance spectroscopy. The compounds behaved as cathodic type inhibitors in the acid solution **(Rafiquee *et al.*, 2007)**.

The effect of Sodium Lauryl sulfate (SLS) on corrosion of mild steel in 1M HCl was studied using weight loss, electrochemical polarization and metallurgical research microscopy. Results obtained revealed the SLS was anodic in nature and showed very good corrosion inhibition efficiency **(Atul Kumar *et al.*, 2008)**

Chemical and electrochemical methods were employed to study the effect of Metol as corrosion inhibitor for steel. It was found that metal inhibition efficiency increased with increase in concentration and electrochemical methods reveal that the inhibitor acted as mixed type inhibitor. SEM confirmed the foramtion of passive film on the metal surface **(Praveen *et al.*, 2009)**.

4-substitued anilinomethylpropionate were synthesized and investigated as corrosion inhibitors for mild steel in 1N HCl solution using weight loss, polarization resistance, Tafel polarization and Electrochemical impedance spectroscopic techniques. Results suggested that all the inhibitors were mixed type in nature **(Sudhish Kumar *et al.*, 2009)**

The corrosion protection mechanisms of carbon steel by an epoxy resin containing indole-3-butyric acid (IBA) was studied by Xuan hang et al using electrochemical impedance measurements. The experiments performed on scratched samples revealed that IBA acted as anodic inhibitors **(Xuan Hang *et al.*, 2010).**

Rajalakshmi *et al.*, (2010) studied the inhibition efficiency of Dicyloimine hydrochloride (DCI) on mild steel in 1M HCl using weight loss method and electrochemical polarization studies. Results revealed that DCI acted as an effective inhibitor in HCl media forming a chemisorbed layer and behaved as a mixed inhibitor.

The inhibitive effect of Chloroquinone phosphate (CQP) for mild steel in 1M HCl in the concentration range of $5x10^{-6}$ M to 1 x 10^{-2} M was studied by weight loss, electrochemical meauremen. CQP yielded 98% in 1M HCl and it was found to behave as a mixed type inhibitor. CQP yielded 98% in 1M HCl and it was found to behave as a mixed type inhibitor. **(Rajalakhsmi *et al.*, 2009).**

Chitra *et al.*, (2010) studied the inhibition efficiency of sulpha Schiff bases using electrochemical and nonelectrochemical techniques. The IE increased with concentration and decreased with temperature. The inhibitors behaved as mixed inhibitors.

Ashish Kumar *et al.*, (2010) analysed the effect of Cefazolin on the corrosion of mild steel in HCl by weight loss, electrochemical impedance spectroscopy and

Potentiodynamic polarization studies. Cefazolin acted as mixed type inhibitor with predominant cathodic nature.

2.8 Nitrogen containing compounds

It is well known that heterocyclic compounds containing nitrogen atoms are good corrosion inhibitors for many metals and alloys in various aggressive media. Nitrogen containing compounds donate lone pair of electrons present on the nitrogen atom and prevent metal corrosion. Nitrogen containg heterocyclic compounds are considered to be effective corrosion inhibitors. N-heterocyclic compound inhibitors acted by adsorption on the metal surface and the adsorption of N-heterocyclic inhibitor took place through nitrogen heteroatom, as well as those with triple or conjugated double bonds or aromatic rings in their molecular structures

The inhibition of corrosion of mild steel in 1M HCl by triazole derivatives was investigated using electrochemical and weight loss measurements. Polarization curves reveal that the triazole derivatives were of mixed type and found to obey Langmuir adsorption isotherm **(El Mehdi *et al.*, 2002)**.

Electrochemical measurements were employed to determine the inhibitive effect of N-phenyl oxalic acid dihydrazide (PODH), oxalic N-phenyl hydrazide (OPHPT), N'-phenyl thiosemicarbazide for the corrosion of mild steel in molar HCl and the inhibition efficiency was found to be 92% for OPHPT and 79% for PODH. Adsorption of these inhibitors on the mild steel surface obeyed Langmuir adsorption isotherm **(Labari *et al.*, 2005).**

Weight loss measurements, potentiodynamic polarization and electrochemical impedance spectroscopy were employed to study the effect of three Schiff base compounds on the corrosion behaviour of steel in 2M HCl solution and the results reveal that an average inhibition efficiency of about 93% could be arrived at 10^{-2} M additive concentration. All the three compounds acted as mixed type inhibitor and obeyed Langmuir adsorption isotherm **(Kaan *et al.*, 2006)**.

Triazole derivative was synthesized and its inhibition action on the corrosion of mild steel in 1M HCl was investigated by means of weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy and scanning electron microscopy. The efficiency attained a maximum of 90-99% and behaved mainly as mixed type inhibitor and the adsorption process was under charge transfer control.

The values of ΔG_{ads} indicated the adsorption was a spontaneous process and followed typical chemisorption **(Fengling *et al.*, 2008)**.

Wei-hua Li *et al.*, (2008) proved that the triazole derivatives 3,4-dichloroaceto phenone-o-1'-(1',3,4,-triazolyl)-methaneoxime(4-DTM) and 2,5-dichloroacetopenone-o-1'(1',3',4'-trizolyl)methaneoxime (5DTM) were good inhibitors for mild steel in acid media. The inhibition effects were investigated using weight loss, Electrochemical impedance spectroscopy and scanning electron microscopy. The results revealed that the inhibitors obey Langmuir adsorption isotherm and the calculated values of ΔG_{ads} were negative

Weight loss and potentiodynamic polarization methods were employed to determine the inhibition effect of 6-benzyl amino pyrine (BAP). Results showed BAP was a good inihibitor and acted as mixed type and obeyed Temkin adsorption **(Xianghong *et al.*, 2009)**.

Bentiss *et.al.*, (2009) studied the inhibition characteristics of 1,3,4-thiadiazole moiety for acid corrosion of carbon steel using electrochemical impedance spectroscopy. The corrosion inhibition was due to the formation of chemisorbed film on the metal surface.

Corrosion inhibitive performance of three amino acids namely L-methionine, L-methionine sulfoxide and L-methionine sulfonate for copper surface in 1.0M nitric acid was investigated. Decrease in corrosion rate was observed for all the investigated compounds **(Khaled , 2010)**.

Ashish Kumar Singh *et al.*, (2010) studied the adsorption and inhibitive effect of cefazolin on mild steel in 1M HCl at 303-338K. The results showed that inhibition efficiency increased with increase of inhibitor concentration. The adsorption obeyed Langmuir adsorption isotherm equation. It acted as mixed type inhibitor and was found to be predominantly cathodic.

2.9 Imidazoline Derivatives as Corrosion Inhibitors

The influence of the 1-hydroxyimidazole-3-N-oxide (HOI), 1-hydroxy-2-benzolyl-5-phenylimidazole-3-N-oxide (HOBFI) and 1-hydroxyimidazolyle-2,4,5-trimethyl-3-N-oxide (HOTM1) in aluminium corrosion in 0.01M NaOH, were investigated using polarization and impedance measurements **(Scholl *et al.*, 1992)**.

An investigation of the mode of action of the corrosion inhibitor oleic imidazoline was carried out using corrosion testing, second harmonic generation at

surfaces and molecular modeling techniques. Selected variations to the molecular structure have been made to elucidate the relevant roles of the constituent parts of the molecule. Results showed that the molecule was primarily bonded through the five-membered nitrogen ring which was lying planar to the metal surface **(Edwards *et al.*, 1994)**.

Three imidazoline derivatives with different electron-releasing substitutents were designed by quantum chemical study. Based on the theoretical and experimental results it was indicated that the electron donor substituent particularly the substituent group with conjugated system, introduced to imidazoline ring will improve inhibition efficiency **(Daxi wang *et al.*, 1999)**.

Electrochemical impedance spectrum, polarization curves, surface analysis techniques were employed to study the inhibition mechanism and adsorption/desorption behaviour of imidazoline amide (IM) on Fe surface in NaCl solutions. The results showed that the adsorption of imidazoline on Fe surface obeyed Langmuir isotherm. The increase in temperature decreased the adsorption potential of the inhibitor on the Fe surface **(Xueyuan *et al.*, 2001)**.

Popova *et al.*, (2003) investigated six benzimidazole derivatives- 2-phenylbenzimidazole, 2-pyridylbenzimidazole, 2-(o-amino)phenylbenzimidazole, 2-Benzylimidazole, 1-Benzylbenzimidazole 1,2-Dibenzylbenzimidazole as corrosion inhibitors on mild steel in 1M HCl using gravimetric and polarization techniques.. The benzimidaozole derivatives studied proved to have good protective properties against corrosion of mild steel in 1M HCl.

Electrochemical testing and SEM analysis were used to study the effect of concentration of four heterocyclic molecules on the corrosion susceptibility of steel pipeline samples. The compounds used were: 2-mercaptobenzimidazole (MBI), 5-mercapto-1-tetrazoleacetic sodium salt (MTAc), 1-hydroxybenztriazole (HBT) and benzimidazole (BIA). The results revealed that a maximum inhibition efficiency of 98% was obtained **(Morales *et al.*, 2004)**.

The electrochemical behaviour of 1-(2-ehtylamino)-2-methyl imidazoline and its derivative was evaluated by using potentiodynamic polarization curves and electrochemical impedance spectroscopy. The experimental results suggest that imidazoline acted as a good corrosion inhibitor at different concentrations **(Cruz *et al.*, 2004)**.

The inhibiting ability of benzimidazole and its derivatives like 2-mercaptobenzimidazole, 2-methylbenzimidzole and benzimidzole against the corrosion of mild steel in 1M HCl solution was studied using polarization and impedance spectroscopic studies. The adsorption of these compounds follow Langmuir adsorption isotherm model. The inhibition efficiency increased with increase in inhibitor concentration **(Aijourani *et al.*, 2009)**.

The acid corrosion inhibition process of mild steel in 1M HCl by 1-butyl-3-methyl imidazolinium chlorides and 1-butyl-3-methyl imidazolium hydrogen sulphate has been investigated using electrochemical impedance, potentiodynamic polarization and weight loss measurements. Potentiodynamic polarization studies indicate that the inhibitors are of mixed type and the adsorption of the inhibitor on the mild steel obeyed the Langmuir adsorption isotherm and the thermodynamic parameters indicate the reaction is spontaneous and the inhibitor is physically adsorbed on the mild steel **(Zhang and Hua, 2009)**.

The corrosion inhibitive nature of a group of benzimidazoles, namely benzimidzole(BIM), 2-hexyl benzimidazole (2-HBIM) and 2-benzyl chloride benzimidazole (2-CIBBIM), was studied using density functional theory. Results reveal that the studied molecules interacted with Fe-atoms mainly in their stable pyridine-N-protonated forms. The C (7) atoms as reactive sites receive electrons from Fe atoms, benzene ring donate electrons to vacant orbital of Fe-atom **(Da-Zhi Li *et al.*, 2010)**.

Cationic surfactants having different alkyl chain lengths were prepared by amidation of lauric, myristic, palmitic, stearic, oleic acids with diethlyene triamine and evaluated as corrosion inhibitor for steel alloy in 1M HCl and H_2SO_4. The results indicated that these materials behaved as good corrosion inhibitors **(Aiad *et al.*, 2010)**.

Weight loss and electrochemical methods were used to study the inhibitive action of 2-mercaptobenthidazole (2MBI) on mild steel in 1M HCl. Adsorption of 2MBI on the mild steel surface in 1M HCl follow Langmuir Adsorption isotherm **(Benabdellah *et al.*, 2011)**.

The study involves the synthesis of O-chlorophenyl-2-imidazoline (OCP2I) and its inhibition behaviour on mild steel corrosion in sulphuric acid and hydrochloric acid media, using weight loss method and electrochemical methods. The results of

weight loss method revealed that, the inhibitor furnished a maximum efficiency of 84.55% in H_2SO_4 at 200 ppm and 91.42% in HCl medium at 120 ppm of concentration. Thermodynamic parameters indicated physisorption mode of adsorption OCP2I followed Langmiur and Temkin adsorption isotherms. Potentiodynamic polarization and impedance studies were conducted to investigate the mechanism of the inhibition and the present system follows mixed mode of inhibition **(Nalini *et al.*, 2011).**

A heterocyclic imidazoline, 3,4,5-Trimethoxy phenyl-2-imidazolines (TMP2I) was tested for its corrosion inhibition in 0.5 M H_2SO_4 and 1M HCl using weight loss, Tafel polarisation and electrochemical impedance techniques. The results showed that the inhibition efficiency increased with the increase in concentration of TMP2I and the higher efficiency of about 98% was obtained in both the acid media at 20ppm. The adsorption of TMP2I obeyed Langmuir adsorption isotherm and was found to occur spontaneously. Cathodic and anodic polarization curves of mild steel in the presence of different concentrations of TMP2I at 30°C reveal that it was a mixed type of inhibitor. The surface morphology of the mild steel specimens was evaluated using SEM images **(Nalini *et al.*, 2011).**

2.10 Quantum chemical studies

Quantum chemical methods are becoming ever more prevalent for assessing surface interactions of different molecules using cluster models and semi-empirical, ab initio Hartree–Fock and density functional theory (DFT) studies considering the standard potential energy surfaces. Molecular modelling has the potential to identify structurally similar compounds worthy of synthesis and subsequent corrosion testing. Thus, if a molecular mechanics model of the interactions that control the adsorption of a minimised structure with a particular metal can be set up, a measure of the binding (docking or adsorption) energy of the molecule with the metal can be calculated. Whilst this binding energy has no absolute meaning, calculating the relative binding energy of a series of structurally similar ligands may lead to the prediction of other related compounds with potentially more effective inhibiting action.

Quantum chemical calculations were performed on four typical amides compounds e.g. urea, thiourea, thioacetamide and thiosemicarbazide, using the semi-empirical method MINDO/3 within program package HyperChem 6.03. Obvious

correlations were found between corrosion inhibition efficiency and some quantum chemical parameters such as highest occupied molecular obital (HOMO), lowest unoccupied molecular orbital (LUMO) energy levels, HOMO–LUMO energy gap and electronic density etc. Calculated results indicate that the great difference of inhibition efficiencies between these amides can be clearly explained in terms of frontier molecular orbital theory. The agreement with the experimental data was also found to be satisfactory **(Jian Fang *et al.*, 2002)**

Inhibition mechanism of five imidazoline derivatives for carbon steel against CO_2 corrosion was studied by molecular modeling. The research by quantum cheimistry revealed that the reactive sites of imidazoline molecules were located at imidazoline ring and these molecules could coordinate and backdonating bonds with atoms on metal surface **(Jun Zhang *et al.*, 2010)**.

Corrosion inhibition performance of 1-hydroxy ethyl-2-heptadecylimidazoline and 1-amionoehtyl-2-heptadecyl imidazoline for mild steel was evaluated by combination of quantum chemistry calculation, molecular mechanics and molecular simulation. The calculated results by quantum chemical methods demonstrated that frontier orbitals are mainly located on imidazoline rings **(Jinxiang *et al.*, 2010)**.

Computational calculations on some piperazine derivatives as corrosion inhibitor for steel in presence of KI in sulphuric acid of different normality in gas and aqueous phases using semi-empirical methods (i.e. MINDO/3, MNDO, PM3 and AM1) were carried out to search possible correlation between corrosion rates and geometric structures, charges on nitrogen atoms, highest occupied molecular energy level (HOMO); lowest unoccupied molecular energy level (LUMO); the differences between highest occupied molecular orbital energies and lowest unoccupied molecular orbital energies (HOMO) and (LUMO) were carried out **(Bereket *et al.*, 2003).**

The anti-corrosive properties of some antipyrine Schiff bases (benzylidine amino)antipyrine (a), 4-hydroxy 3-(benzylidine amino)antipyrine (b), 2-hydroxy 3-(benzylidine amino)antipyrine (c), and 2-hydroxy 3-(naphthylidine amino)antipyrine (d) were studied using density functional theory at the B3LYP/6- 31G level. The computational calculations were performed to find a relation between their electronic and structural properties and the inhibition efficiency. The calculated quantum chemical parameters correlated to the inhibition efficiency are, the highest occupied

molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), the separation energy (DE), the dipole moment (m), the softness (s), the total negative charge on the whole molecule (TNC), the total charge on the azomethine moiety, the molecular volume (Vi), and the total energy (TE). A good correlation between the quantum chemical parameters and the experimental inhibition efficiency was found **(Issa *et al*, 2010)**.

Semi-empirical quantum chemical calculations were used to study the interaction of positively charged amino acids (lysine, arginine or histidine) with a homologue set of n-alkyl sulfate derivatives in the gas and aqueous phase. Full geometry optimization of the amino acids and surfactants were achieved by means of AM1 and PM3 calculation methods in which the latter gave more reasonable results. Amino acids were considered as zwitterionic and coated forms. In the latter forms, the amine and carboxyl groups of amino acids were protected by the formyl and amine groups, respectively. Enthalpy differences of the reactions were calculated and compared with the experimental results obtained by other workers. Gas phase calculations showed that by increasing the number of carbon chain length of surfactants, DH of the reaction will be more endothermic, while the experimental data showed a reverse behavior. However, the trend of DH of reaction vs. number of carbon atoms in the surfactants tail, obtained by aqueous phase calculations, was in direct agreement with the experimental results. **(Motamedi *et al.*,2004).**

The electronic and molecular structure of several heterocyclic organic compounds: 1,3,4-thiadiazole and its derivatives, with different nucleophilic and electrophilic alkyl substituents (R1 and R2), obtained through quantum-chemistry calculations conducted by means of the GAUSSIAN 03W set of programs. The reactive sites of these derivatives were located mainly in the N2 and N3 pertaining to the ring of thiadiazole, with the exception of the derivatives 5, 8 and 9 that present other reactive sites of importance in atoms of nitrogen, sulfur and chlorine **(Luz Marı *et al.*,2005).**

The effects of thiourea (TU), methylthiourea (MTU) and phenylthiourea (PTU) on the corrosion behaviour of mild steel in 0.1 M H_2SO_4 solution was investigated using the techniques of R_p (polarisation resistance) and EIS (electrochemical impedance spectroscopy). These compounds exert a good corrosion inhibition property, phenylthiourea being the most efficient and thiourea the least. The

effect of molecular structure on the inhibition efficiency on corrosion had been investigated by ab initio quantum chemical calculations. The electronic properties such as highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy levels, LUMO–HOMO energy gap and molecular orbital densities were calculatedThe highest values of the HOMO densities were found in the vicinity of the sulphur atom indicating it as most probable adsorption centre **(M. O¨ zcan *et al.*,2004)**

Corrosion inhibitive performance of 2-aminopyrimidine (APr), 2,4-diaminopyrimidine (dAPr), 2,4-diamino- 6-hydroxy-pyrimidine (dAHPr) and 2,4,6-triaminopyrimidine (tAPr) during the acidic corrosion of steel surface was investigated using three methods, MP2, ab initio Hartree–Fock and density functional theory (DFT). Quantum chemical parameters revealed a good correlation between the theoretical data and the experimental results **(Jamalizadeh *et al.*, 2008).**

A molecular dynamics study for the adsorption of three benzimidazole derivatives and their inhibition characteristics was studied using chemical (weight loss) and electrochemical measurements (potentiodynamic polarization and electrochemical impedance spectroscopy, EIS). Results obtained from weight loss, D.C polarization and A.C impedance measurements were in reasonably good agreement and show increased inhibitor efficiency with increasing inhibitor concentration. The molecular dynamics study revealed that the benzimidazole ring as well as the side chain acts as the active sites in these inhibitors and they can absorb on Fe surface by donating electrons to iron d-orbital (**Khaled *et al.*, 2010).**

The corrosion inhibition behaviour of four selected amino acid compounds, namely L-cysteine, L-histidine, L-tryptophan and L-serine on mild steel surface in deaerated 1 M HCl solution were studied electrochemically by Tafel polarization and electrochemical impedance spectroscopy methods and computationally by the quantum chemical calculation and molecular dynamics simulation. Electrochemical results show that these amino acid compounds inhibit the corrosion of mild steel in 1 M HCl solution significantly. The quantum chemical calculations were performed to characterize the electronic parameters which are associated with inhibition efficiency. The molecular dynamics simulations were applied to find the equilibrium adsorption configurations and calculate the interaction energy between inhibitors and iron

surface. The electrochemical experimental results are supported by the theoretical data **(Jia-jun Fu *et al.*, 2010).**

The inhibitive action of some benzimidazole derivatives namely 2-(2-furanyl)-1H-benzimidazole (FB), 2-(2-pyridyl) benzimidazole (PB) and 2-(4-thiazolyl) benzimidazole (TB), against the corrosion of iron in solutions of nitric acid has been studied using density function theory calculations (DFT), weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The calculated electronic parameters involved in the activity of the benzimidazole derivatives confirmed that the position of the side chain in the benzimidazole moiety affected the pattern of activity. The inhibition efficiency increased with the increase in E_{HOMO} and decrease in E_{LUMO}–E_{HOMO}. TB had the highest inhibition efficiency because it had the highest HOMO energy and ΔN values, and it was most capable of offering electrons.The effectiveness of the benzimidazole derivatives followed the order TB > PB > FB. The same order was supported by the experimental chemical and electrochemical measurements. **(Khaled *et al.*, 2010).**

Thorough analysis of the literature survey reveals that imidazoline derivatives **P2I, TMP2I, DMP2I, OCP2I, PNDMP2I and PNP2I** have not yet been reported as corrosion inhibitors for mild steel in acid media.

The methodology adopted in this investigation is clearly presented in the **Chapter III.**