CHAPTER – 9
SUMMARY AND CONCLUSIONS

The importance of corrosion studies is of threefold. The first area of significance is economic, including objective of reducing losses resulting from corrosion of tanks, metal components of machine, ships, bridges and so on. The second area, is improving safety of operating equipments which due to corrosion may fail with catastrophic consequences. The third objective is conservation, applied primarily to metal resources, the world's supply of which is limited and the wastage of them includes corresponding loss of energy and water reserves associated with the production and fabrication of metal structures.

The corrosion control of metals is an important activity of technical, economical, environmental and aesthetical importance. Mild steel is the material of wide industrial application due to its relatively low cost compared to other metals and alloys. The study of corrosion of mild steel in acid media is both of academic and industrial concern that has received a considerable amount of attention. Mild steel has been extensively used under different conditions in chemical and allied industries in handling alkalies, acid and salt solutions. It suffers severe corrosion in these aggressive environment from which is to be protected. Hence, the study of corrosion inhibition of mild steel (MS) in aqueous aggressive media is the subject of pronounced technological significance. Thus the investigation has been carried out with mild steel.

The present study was aimed to investigate the protection performance of isoxazolines, hydroxy pyrazolines, pyrimidines and bispyrazoles, bis-isoxazoles, bispyrimidines from chalcones on mild steel corrosion in sulphuric acid medium. The discussions made in the various chapters have been summarized below:

The introductory aspects of the present investigation have been presented as three parts in Chapter 1. Part I deals with civilization, definition, historical background of corrosion, importance of corrosion studies, classification, principles, theories of corrosion and different forms of corrosion.

A general account of corrosion inhibitors which includes definition and classification of inhibitors in the field of corrosion, theories of adsorption of inhibitors

such as physisorption and chemisorption, factors affecting the applicability of inhibitors, adsorption isotherms and various mechanisms of corrosion inhibition have been presented in part II.

The third part deals with various corrosion monitoring techniques that are generally employed for the detection and measurement of corrosion and corrosion inhibition. It discusses the principle and application of the following monitoring techniques, *viz.*, physico-chemical method includes weight loss method (coupon method) and gasometric method, electrochemical method includes Tafel polarization, linear polarization and AC- impedance methods. The methods of deriving the various corrosion kinetic parameters viz., percentage inhibition efficiency (%), surface coverage (θ), corrosion rate (C_R), Tafel slopes (b_a and b_c), corrosion current density (I_{corr}), corrosion potential (E_{corr}), charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) have been neatly presented in this chapter. A brief introduction on application of chalcones in heterocyclic synthesis has also been incorporated.

Chapter 2 deals with the previous work done with nitrogen, oxygen and sulphur containing heterocycles as corrosion inhibitors for mild steel in acidic media.

The work embodied in the present thesis deals with the study of some nitrogen, oxygen and sulphur containing heterocycles as corrosion inhibitors for mild steel in 1M H_2SO_4. The performances of all the synthesized compounds have been investigated using laboratory corrosion immersion techniques and electrochemical methods like electrochemical impedance spectroscopy and Tafel polarization method. FTIR spectroscopy, scanning electron microscopy-energy dispersive X-ray analysis (SEM - EDS), atomic force microscopy (AFM) and X-ray diffraction techniques (XRD) have also been used to examine the inhibitive performance of some selected compounds. Quantum chemical calculations have also been performed using DFT in aqueous phase for some selected compounds in both non-protonated and protonated forms. The compounds examined in the present investigations and their inhibiting action has been discussed in the chapters-3, 4, 5 and 6.

Chapter 3 deals with the experimental details regarding the metal used for the study, electrode preparation and the reagents used. The synthesized compounds used are as follows

ISO 1 - 3-phenylamino-5-phenylisoxazoline

ISO 2 - 3-phenylamino-5-(3′,4′,5′-trimethoxyphenyl)isoxazoline

ISO 3 - 3-phenylamino-5-(3′-methoxy-4′-hydroxyphenyl)isoxazoline

ISO 4 - 3-phenylamino-5-(3′,4′-dimethoxyphenyl)isoxazoline

ISO 5 - (3-phenylamino-5-(2′-nitrophenyl)isoxazoline

ISO 6 - 3-phenylamino-5-(4′-dimethylaminophenyl)isoxazoline

ISO 7 - 3-phenylamino-5-(4′-methoxyphenyl)isoxazoline

ISO 8 - 3-phenylamino-5-(2′-hydroxynaphthyl)isoxazoline

ISO 9 - 3-phenylamino-5-(4′-hydroxyphenyl)isoxazoline

ISO 10 - 3-phenylamino-5-(4′-chlorophenyl)isoxazoline

Investigations were carried out with mild steel specimens of composition 0.084% C, 0.369% Mn, 0.129% Si, 0.025% P, 0.027% S, 0.022% Cr, 0.011% Mo, 0.013% Ni and 99.32% Fe. Various experimental techniques employed for the study of corrosion and its inhibition have been presented. The results of the investigations in chapter III revealed that isoxazoline and its derivatives inhibit the corrosion of mild steel effectively in 1M H_2SO_4 solution at all the studied concentrations (0.5 - 10 mM). Maximum inhibition efficiency was achieved at a concentration of 10 mM. ISO 8 exhibited the highest percentage inhibition efficiency (98 %). Determination of various corrosion parameters such as surface coverage (θ), corrosion rate (CR), inhibition efficiency (% IE), energy of activation (E_a), thermodynamic parameters (ΔG°_{ads} , ΔH°_{ads} , ΔS°_{ads}), corrosion potential (E_{corr}), corrosion current density (I_{corr}), Tafel slopes (b_a and b_c), charge transfer resistance (R_{ct}), and double layer capacitance (C_{dl}) have been explained. Polarization studies showed that all the isoxazolines function as mixed inhibitors but predominantly cathodic in nature.

Using the Gaussian software, quantum chemical calculations have been performed and discussed. Various quantum chemical parameters such as the energy of the highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment

(μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), the fraction of electrons transferred (ΔN), total energy (TE) and Mulliken atomic charges have been evaluated to characterize the inhibition property of the inhibitors. Results obtained from quantum chemical studies for some of the protonated isoxazoline derivatives were found to be in good agreement with the experimental results.

In chapter 4, the results of the inhibition efficiency of hydroxy pyrazolines have been presented. The compounds used for the investigation in this chapter are:

PPM - [5-hydroxy-3-phenyl-5-(phenylamino)-4,5-dihydro-1*H*-pyrazol-1-yl] (phenyl)methanone

PHPM - (2-hydroxyphenyl)[5-hydroxy-3-phenyl-5-(phenylamino)-4,5-dihydro-1*H*-pyrazol-1-yl]methanone

PAPM - (2-aminophenyl)[5-hydroxy-3-phenyl-5-(phenylamino)-4,5-dihydro-1*H*-pyrazol-1-yl]methanone

PNPM - [5-hydroxy-3-phenyl-5-(phenylamino)-4,5-dihydro-1*H*-pyrazol-1-yl](3-nitrophenyl)methanone

PCT - 5-hydroxy-3-phenyl-5-(phenylamino)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide

PPCT - 5-hydroxy-N,3-diphenyl-5-(phenylamino)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide

Results reveal that all the six hydroxy pyrazolines act as good corrosion inhibitors having efficiency of 80 to 99 % at a concentration of 10 mM towards mild steel in 1M H_2SO_4 solution. The highest inhibition efficiency of these compounds was attributed to the presence of π-electrons on the pyrazole and benzene rings, -NH, >C=N-, C=O, -OH and NH_2 groups which enhances the electron density of the aromatic ring leading to greater adsorption.

Adsorption of all the inhibitors on mild steel surface followed Langmuir adsorption isotherm. The amount of dissolved iron in the presence and absence of inhibitors determined by AAS coincided with weight loss data. FTIR, SEM - EDS, XRD and AFM spectra revealed the formation of a smooth, dense protective layer on the mild steel surface.

In Chapter 5 the effect of introducing –OH, -SH functionalities, furan and pyridine rings on the corrosion inhibition efficiency of pyrimidines and azoles have been presented. The compounds employed in this chapter are:

FPH - 4-(furan-2-yl)-6-phenylpyrimidin-2-ol

FPT - 4-(furan-2-yl)-6-phenylpyrimidine-2-thiol

FPO - 5-(furan-2-yl)-3-phenyl-4,5-dihydro-1,2-oxazole

FPP - 5-(furan-2-yl)-3-phenyl-4,5-dihydro-1*H*-pyrazole

PPH - 4-phenyl-6-(pyridin-2-yl)pyrimidin-2-ol

PPT - 4-phenyl-6-(pyridin-2-yl)pyrimidine-2-thiol

POP - 2-(3-phenyl-4,5-dihydro-1,2-oxazol-5-yl)pyridine

PPP - 2-(3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)pyridine

The inhibitors with pyrimidine ring exhibited maximum inhibition efficiency. The effect of temperature on the inhibition efficiency was examined and some thermodynamic parameters were computed. A probable inhibitive mechanism was proposed to explain the results.

In chapter 6, inhibition performance of bis-isoxazoles, bis-pyrazoles and bis-pyrimidines have been evaluated for their corrosion inhibition properties by various corrosion monitoring techniques. The synthesized bis-compounds used for the investigation in this chapter are:

BPH - 4,4'-benzene-1,4-diylbis(6-phenylpyrimidin-2-ol)

BPT - 4,4'-benzene-1,4-diylbis(6-phenylpyrimidine-2-thiol)

BPO - 3,3'-benzene-1,4-diylbis(5-phenyl-4,5-dihydro-1,2-oxazole)

BPP - 3,3'-benzene-1,4-diylbis(5-phenyl-4,5-dihydro-1*H*-pyrazole)

BPPH - 4,4'-benzene-1,4-diylbis[6-(pyridin-3-yl)pyrimidin-2-ol]

BPTT - 4,4'-benzene-1,4-diylbis[6-(pyridin-3-yl)pyrimidine-2-thiol]

BPPO - 3,3'-[benzene-1,4-diylbis(4,5-dihydro-1,2-oxazole-3,5-diyl)]dipyridine

BPPP - 3,3'-[benzene-1,4-diylbis(4,5-dihydro-1*H*-pyrazole-3,5-diyl)]dipyridine

DTPH - 5-(2,5-dimethylthiophen-3yl)-4-(4-(6-(2,5-dimethylthiophen-3-yl)-2-hydroxypyrimidin-4-yl)phenyl)pyrimidin-2-ol

DTPT - 5-(2,5-dimethylthiophen-3yl)-4-(4-(6-(2,5-dimethylthiophen-3-yl)-2-mercaptopyrimidin-4-yl)phenyl)pyrimidin-2-thiol

DTPO - 5-(2,5-dimethylthiophen-3yl)-4-(4-(5-(2,5-dimethylthiophen-3-yl)-4,5-dihydroisoxazol-3-yl)-4,5-dihydroisoxazole

DTPP - 5-(2,5-dimethylthiophen-3yl)-4-(4-(6-(2,5-dimethylthiophen-3-yl)-4,5-dihydro-1H-pyrazol-3-yl)-4,5-dihydro-1H-pyrazole

In all the three classes of compounds, the compounds with pyrimidine nucleus containing –SH group exhibited maximum inhibition efficiency of 99.03 %, 93.05 % and 84.02 %. The results of weight loss and electrochemical measurements showed that all the three classes of compounds have an excellent inhibiting property for acidic corrosion of mild steel. Adsorption of all the inhibitors on mild steel surface followed Langmuir adsorption isotherm. The SEM-EDS, FTIR, XRD and AFM studies confirmed the formation of protective layer on the mild steel surface. There was a strong correlation between experimental inhibition efficiencies and some quantum chemical parameters namely, E_{HOMO}, E_{LUMO}, ΔE and ΔN in protonated form.

The effect of change in the nature of aggressive medium on the inhibition efficiency of the inhibitors has been dealt in Chapter 7. The best inhibitor (ISO 8, PPCT, PPT and DTPT) in each series was selected and their inhibition efficiency in 2M HCl was compared and evaluated by electrochemical and non-electrochemical techniques.

Chapter 8 was aimed to study the synergistic effect of halide ions (Cl^-, Br^- & I^-), surfactants (cetyltrimethylammoniumbromide (CTAB) and sodiumlaurylsulphate (SLS) on isoxazolines and hydroxy pyrazolines in 1M H_2SO_4 by weight loss method. A thorough survey of literature revealed limited work has been reported so far on the synergistic effect of halide ions and surfactants in combination with inhibitors. The synergistic influence has been found to follow the order $I^- > Br^- > Cl^-$ and for surfactants CTAB > SLS. The adsorption of inhibitors obeyed Langmuir adsorption isotherm and the value of ΔG°_{ads} confirmed mixed type of adsorption involving both physisorption and chemisorption.

Chapter 9 deals with summary and conclusions arrived from the above chapters and finally the scope for future research in this field is presented in chapter 10.