CHAPTER VII

SUMMARY AND CONCLUSIONS

Corrosion is a crucial problem in industrial sectors leading to disasters and economic loss. It damages the quality, durability and efficiency of the industrial equipments and infrastructure. Mild steel a versatile material, plays a significant role in variety of industries including chemical reactors, storage tanks, boilers, petroleum industries etc., due to their outstanding mechanical and structural properties. Inorganic acids such as sulphuric acid, hydrochloric acid are widely utilised for acid pickling and chemical cleaning of metals. Ultimately the usage of mineral acids results in corroding the metal. Effective methods to mitigate corrosion are barrier coatings, hot-dip galvanisation, cathodic protection, material selection, inhibitors etc., Among the various methods, usage of corrosion inhibitors is a convenient method to inhibit corrosion. Inhibitors possess hetero atoms like S, N, O, aromatic rings, double bonds in their structure that acts as important centres for adsorption leading to form a protective layer on the surface of the metal and reduce corrosion rate. Thus our motto is to find a green, eco-friendly inhibitor to mitigate corrosion. Based on this aspect, the present work has been chosen to explore the support of natural as well as synthetic inhibitors in shielding the metal specimens in corrosive medium. The discussions in various chapters are summarized below,

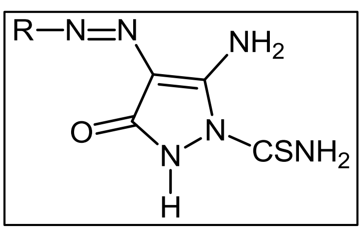
The introduction part of the present research is detailed in **chapter I** which comprises of causes, effects, factors influencing and mechanism of corrosion. Different types of inhibitors are presented. The corrosion monitoring techniques used to measure the corrosion process was also discussed.

The report in **chapter II** continues to focus on the application of green inhibitors such as *Senna auriculata*, *Rosa damascena*, *Cyperus rotundus* and *Cissus quadrangularis* as corrosion mitigators for mild steel in 0.5 M H_2SO_4. The acid and ethanol extracts of the above mentioned green compounds were prepared. The active phytochemical compounds present in the extracts were analysed by GC-MS analysis. The functional groups present in the inhibitors were recorded by FT-IR spectra. The protection efficiency for different concentrations (2, 4, 6, 8, 10, 12 v/v%) were obtained from the mass loss method and the effectiveness of the inhibitor increased with increase in concentration. Based on the mass loss measurements, the order of % inhibition efficiency was SAEE > RDAE > CREE > SAAE > RDEE > CQAE> CRAE> CQEE. The superior inhibition efficiency was for SAEE with 93.94 %. Best fit of the experimental results was observed for Langmuir adsorption isotherm. The effect of temperature on corrosion behaviour in presence of inhibitors was studied in the range 303 K-333 K and the results supported physisorption process. Activation and thermodynamic parameters involved in the adsorption process were calculated and detailed. EIS measurements carried out for selected concentrations (2, 6, 12 v/v%) of the inhibitors revealed an increment in charge transfer resistance as concentration was increased. A mixed inhibition behaviour was proposed for the studied inhibitors by potentiodynamic polarisation techniques. XRD, XPS, SEM-EDS and AFM techniques have been utilised for investigating the surface morphology of mild steel exposed to 0.5 M H_2SO_4 in the absence and presence of inhibitor. The probable mechanism involved in protecting the metal was also detailed. Images of plant inhibitors are presented below.

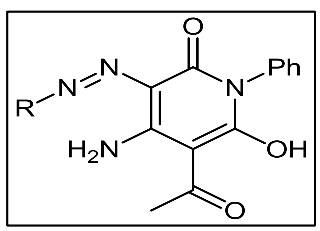



Senna auriculata *Rosa damascena* *Cyperus rotundus* *Cissus quadrangularis*

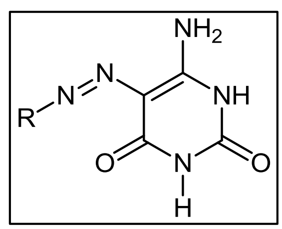
In **Chapter III** a series of sulphamethazine derivatives namely 5-Amino-1-carbothioamido-4-{[4-N-(4,6-dimethyl-pyrimidin-2-yl)sulfamoyl]phenylazo}-pyrazol-5(2H)-one [ACDP] , 5-Acetyl-4-amino-3-{[4-N-(4,6-dimethylpyrimidin-2-yl)sulfamoyl] phenyl azo}-6-hydroxy -1-phenylpyridin-2(1H)-one [ADSH], of 6-Amino-5-{[4-N-(4,6-dimethylpyrimidin-2-yl)sulfamoyal]phenyl azo}-pyrimidine-2,4-(1H,3H)-dione [ADSD], Synthesis of 3-Amino-4-{[4-N-(4,6-dimethylpyrimidin-2-yl)sulfamoyl]phenylazo}–isooxazol-5(2H)one [ADSI], 5-Acetyl-4-amino-3-{[4-N-(4,6-dimethylpyrimidin-2-yl)sulfamoyl] phenylazo}-6-methyl-2H-pyran-2-one [ADSP] were prepared by energy efficient microwave irradiation method has been reported. The spectral analysis including FT-IR, ^{1}H-NMR and ^{13}C-NMR were used to characterise the synthesised compounds. The efficiency of the synthesised compounds as corrosion inhibitors on mild steel in 0.5 M H_2SO_4 was investigated by weight loss technique of concentration (1, 2, 3, 4, 5 mM) at a temperature range 303 K - 333 K. The adsorption of the studied compounds followed Langmuir isotherm model. The enthalpy of activation (E_a) and thermodynamic parameters (ΔH^o and ΔS^o) were determined and discussed. Selected concentration of the inhibitors (1, 3, 5 mM) were chosen for electrochemical measurements. In EIS, changes in impedance parameters (R_{ct} and C_{dl}) with the addition of inhibitors were noticed and PDP studies revealed the mixed nature of the corrosion inhibitors. The order of potency from weight loss method and electrochemical measurements were as follows ACDP > ADSH > ADSD > ADSI > ADSP. All compounds exhibited a maximum protection efficiency of above 90%. In addition to this, ACDP was superior than other compounds with protection efficiency of 96.14% due to the presence of sulphur and nitrogen atoms in the pyrazoles which rises the electron donating ability. The surface properties were investigated by XRD, XPS, SEM-EDS, AFM techniques. Quantum chemical parameters were calculated using density functional theory (DFT) method for the synthesised compounds. Higher E_{HOMO} and lower E_{LUMO} ultimately increased the binding nature of the active molecules on the metal surface. Protonated system followed the same trend in terms of energy gap, HOMO, LUMO, softness, hardness which provided a reasonable support to the experimental findings. The structure of the synthesised compounds are presented below,



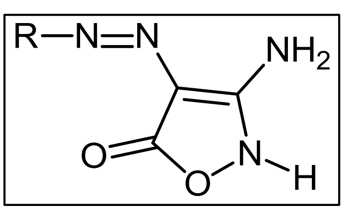
ACDP



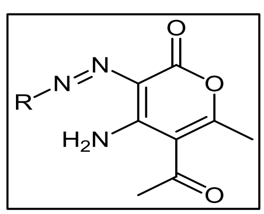
ADSH



ADSD



ADSI



ADSP

Chapter IV deals with the electrochemical behaviour of selected natural (*Rosa damascena* and *Cyperus rotundus*) and synthetic inhibitors (substituted pyrazoles and pyrimidines) on steel rebar in simulated pore solution. The EIS measurements suggested that added inhibitor increased the R_{ct} value. In PDP decrease in I_{corr} value as concentration increased indicated the effectiveness of the inhibitor. The inhibition efficiency based on electrochemical measurements for the studied natural inhibitors were in the order of RDAE > CREE > RDEE > CRAE and synthetic inhibitors are ACDP > ADSD. The studied inhibitors followed Langmuir adsorption isotherm with R^2 value nearer to unity. SEM images supports the formation of adherent layer (protection area) in the presence of inhibitor. The elemental composition of the uninhibited and inhibited metal surface was analysed by EDS. AFM established a highly rough surface in the absence of inhibitor whereas the roughness is reduced in the inhibited systems.

Chapter V deals with the incorporation of green inhibitor (*Senna auriculata*) into nanoclay and dispersed in epoxy resin. The biocompatible components in water extract of *Senna auriculata* was identified by GC-MS analysis. IR spectra evidenced the modified nanoclay. The corrosion resistance of inhibitor coated mild steel was analysed in 0.5 M H_2SO_4 and 0.5 M NaCl by electrochemical measurements. SA-clay epoxy systems showed better results in alkaline than acid medium. SEM images evinced the formation of protective layer.

Chapter VI investigates the degradation behaviour of Ti-6Al-4V alloy in simulated body fluid in the absence and presence of selected natural inhibitors (*Rosa damascena* and *Cissus quadrangularis*). The water extracts of the inhibitors were characterized by GC-MS and IR analysis. Impedance measurements were carried out for the selected concentrations of 2, 6, 12 v/v% of CQWE and RDWE. Addition of inhibitors resulted in increase in R_{in} (inner compact layer resistance). SEM and AFM analysis was performed to examine the effect of inhibitor on its surface property. SEM images indicated surface coverage due to the adsorption of the inhibitor. The composition of elements in the absence and presence of inhibitor was analysed by EDS. AFM studies specified the reduction in average roughness in presence of inhibitor portraying that added inhibitor adhered on Ti alloy.

The insights gained from various methodologies are very important to understand that the natural and synthetic inhibitors acted as a potential corrosion mitigator for mild steel, steel rebar and Ti-6Al-4V in different environments.

Summary and conclusions for all chapters are discussed in **chapter VII** and scope for future work summarised in **chapter VIII**.