

CHAPTER 4

SUMMARY AND CONCLUSIONS

4.1. Summary

Corrosion is a major problem in several industries. It causes enormous wastes of materials which lead to heavy economic losses all over the world. The global economic losses due to corrosion are about US \$2.5 trillion dollars. Among different available methods, the use of corrosion inhibitors is one of the most appropriate, effective and economic ways of mitigating corrosion.

The research work of the present thesis mainly focuses on corrosion inhibition of mild steel in 1M hydrochloric acid solution by thirteen heterocyclic compounds containing different hetero-atoms such as nitrogen, oxygen and sulfur. The corrosion inhibition property of these heterocyclic compounds was evaluated using weight loss, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM), quantum chemical calculations and molecular dynamics techniques. The thirteen heterocyclic inhibitors used in the present investigation have been discussed in four sections. The inhibitors in each section are given bellows:

(a) 5-arylpyrimido-[4, 5-b] quinoline-diones as corrosion inhibitors (APQDs)

- (i) 5-(4-nitrophenyl)-5,10-dihydropyrimido [4,5-b]quinoline-2,4(1H,3H)-dione (**APQD-1**)
- (ii) 5-phenyl-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione (**APQD-2**)

(iii) 5-(4-hydroxyphenyl)-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione (**APQD-3**)

(iv) 5-(2,4-dihydroxyphenyl)-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione (**APQD-4**)

(b) 2-amino-4-arylquinoline-3-carbonitriles as corrosion inhibitors (AACs)

(i) 2-amino-4-(4-nitrophenyl) quinoline-3-carbonitrile (**AAC-1**)

(ii) 2-amino-4-phenylquinoline-3-carbonitrile (**AAC-2**) and

(iii) 2-amino-4-(4-hydroxyphenyl) quinoline-3-carbonitrile (**AAC-3**)

(c) 2, 4-diamino-5-(phenylthio)-5H-chromeno [2, 3-b] pyridine-3-carbonitriles as corrosion inhibitors (DHPCs)

(i) 2,4-diamino-7-nitro-5-(phenylthio)-5H-chromeno[2,3-b]pyridine-3-carbonitrile (**DHPC-1**)

(ii) 2,4-diamino-5-(phenylthio)-5H-chromeno[2,3-b]pyridine-3-carbonitrile (**DHPC-2**)

(iii) 2,4-diamino-7-hydroxy-5-(phenylthio)-5H-chromeno[2,3-b]pyridine-3-carbonitrile (**DHPC-3**)

(d) 3-amino alkylated indoles as corrosion inhibitors (AAIs)

(i) N-((1H-indol-3-yl)(phenyl)methyl)-N-ethylethanamine (**AAI-1**)

(ii) 3-(phenyl(pyrrolidin-1-yl)methyl)-1H-indole (**AAI-2**)

(iii) 3-(phenyl(piperidin-1-yl)methyl)-1H-indole (**AAI-3**)

The 5-arylpymido-[4, 5-b] quinoline-diones (APQDs), exhibited high inhibition efficiency for mild steel corrosion in 1M HCl solution. Results showed that inhibition

efficiencies ($\eta\%$) of the four studied heterocyclic inhibitors at their optimum concentrations (20 mgL^{-1}) obeyed the following order:

$$\text{APQD-4 (97.82\%)} > \text{APQD-3 (96.52\%)} > \text{APQD-2 (95.21\%)} > \text{APQD-1 (92.17\%)}$$

The lower inhibition efficiency of the APQD-1 could be as a result of electron withdrawing nature of the nitrophenyl group at position 5 of the pyrimido-quinoline-dione ring, which decreases the electron density on the adjacent phenyl rings. Conversely, the high inhibition performances of the APQD-3 and APQD-4 can be attributed to the electron releasing effect of the hydroxyl phenyl group(s) at position 5 of the pyrimido-quinoline-dione ring. The highest inhibition efficiency of APQD-4 is attributed due to the presence of two hydroxyl groups at second and fourth position of the aromatic moiety. Adsorption of these compounds over the metallic surface obeyed the Langmuir adsorption isotherm. The higher values of E_a suggested that more energy barrier have been achieved in presence of inhibitors and the rate of mild steel dissolution is reduced due to the formation of inhibitors-Fe complex. The large negative values of ΔG^0_{ads} ($-33.31 \text{ kJmol}^{-1}$ to $-38.19 \text{ kJ mol}^{-1}$) for the investigated inhibitors suggest that the inhibitors adsorb spontaneously on mild steel surface. Potentiodynamic polarization results showed that studied compounds act as mixed-type inhibitors but predominantly act as cathodic inhibitors. The EIS results revealed that values of R_{ct} increased while values of C_{dl} are decreased in presence of inhibitor molecules which is attributed due to adsorption of inhibitors over metallic surface. SEM and AFM analyses further supported the formation of protective film. Quantum chemical calculations revealed that the mode of adsorption of the studied molecules on the steel surface is predominantly via electron donation from the high electron density sites of the molecules to the iron, and this is influenced by the nature of the substituent groups present in the APQDs: the electron density

of the HOMO is delocalized over the entire molecules in APQD-3 and APQD-4 due to presence of electron releasing –OH group(s) and the converse is true for APQD-1 and APQD-2. The Fukui indices revealed the prospective sites for nucleophilic and electrophilic attack in the studied APQDs such that the N- and O- atoms in the molecules except the nitro group in APQD-1 showed high chances of nucleophilic interactions with charged metal surfaces. The MD simulations revealed that the studied compounds adsorbed on Fe surface in a flat or parallel orientation through several potential binding sites, and the calculated values of E_{binding} are essentially high and assumed the same trend as the experimental inhibition efficiencies.

Results showed that inhibition efficiencies ($\eta\%$) of the three studied 2-amino-4-aryl quinoline -3-carbonitriles (AACs) at their optimum concentration (40 mgL^{-1}) obeyed the following order:

$$\text{AAC-3 (96.52\%)} > \text{AAC-2 (95.65\%)} > \text{AAC-1 (94.78\%)}$$

The lower inhibition efficiency of AAC-1 as compared to the other two compounds is attributed due to highly electron-withdrawing effect of the nitro group, while highest inhibition efficiency of AAC-3 is attributed due to electron releasing hydroxyl (-OH) group. The weight loss and electrochemical results suggest that the inhibition efficiency increases with increasing AACs concentrations. The EIS plots suggest that charge-transfer resistance of the corrosion process increases on increasing AACs concentration due to adsorption of these inhibitors at metal / electrolyte interfaces. The adsorption of the AACs on the mild steel surface obeyed the Langmuir adsorption isotherm. The values of activation energies suggested that AACs inhibit mild steel corrosion by forming a protective surface film at metal/ electrolyte interfaces. The large negative values of ΔG_{ads}^0 for the investigated

inhibitors suggest that the inhibitors can adsorb spontaneously on mild steel surface to form highly stable adsorption film. The adsorbed layer of the AACs over the surface of mild steel has been furthermore conformed by SEM, EDX and AFM analysis. The experimental results were well supported by quantum chemical calculations.

The inhibition efficiencies of three studied 2,4-diamino-5-(phenylthio)-5H-chromeno [2, 3-b] pyridine-3-carbonitriles (DHPCs) at their optimum concentration (50 mgL⁻¹/ 12.70 x 10⁻⁵ molL⁻¹) follows the order:

$$\text{DHPC-3 (96.69\%)} > \text{DHPC-2 (96.60\%)} > \text{DHPC-1 (95.30\%)}$$

All the studied DHPCs act as good corrosion inhibitors and their inhibition efficiency increases with increase in concentration, and decrease with increase in temperature. The highest inhibition efficiency of the DHPC-3 among the studied inhibitors is attributed to the presence of the electron donating –OH group at position seven of the chromenopyridine ring. The studied inhibitors significantly elevate the activation energy associated with corrosion reaction and thereby reduce the reaction rate. The large negative values of ΔG_{ads}^0 for the investigated inhibitors suggest that the inhibitors can adsorb spontaneously on mild steel surface to form highly stable adsorption film. Polarization study revealed that studied compounds are mixed type inhibitors with predominantly cathodic inhibitive capacity. EIS study revealed that values of charge transfer resistance (R_{ct}) increases in presence of inhibitors due to the adsorption of inhibitors at metal/electrolyte interfaces. The adsorption of DHPCs on mild steel surface obeys the Langmuir adsorption isotherm and involves physisorption and chemisorption mechanisms. Quantum chemical calculations provide successful explanations to the observed inhibition efficiencies of the molecules based on the frontier molecular energy parameters. The electrophilic and nucleophilic sites of the inhibitor

molecules were identified by Fukui functions. The molecular dynamics simulation study revealed that all the studied inhibitors spontaneously and strongly adsorbed on the Fe (110) surface by flat or parallel orientation and the trend of predicted binding energies agree with experimental inhibition efficiencies.

The inhibition efficiencies of three studied 3-amino alkylated indoles (AAIs) at their optimum concentration (250 mgL^{-1} / 0.862 mM) follow the order:

$$\text{AAI-3 (96.95\%)} > \text{AAI-2 (96.08\%)} > \text{AAI-1 (94.34\%)}$$

The results of both gravimetric and electrochemical experiments showed that all the three compounds inhibit mild steel corrosion in 1 M HCl solution and the inhibition efficiency increases with increasing concentration of the inhibitors. The adsorption of studied AAIs obeys the Langmuir isotherm and involves competitive physisorption and chemisorption modes. Potentiodynamic polarization studies acted as cathodic type inhibitors. The EIS measurements showed that the compounds adsorb on mild steel surface to form protective film with essentially capacitive behaviour. Surface morphology studies using SEM and AFM also provided some evidence of formation of protective film of AAIs on the steel surface. Quantum chemical parameters suggested the inhibition of mild steel corrosion in 1 M HCl solution by the studied compounds is essentially due to effective transfer of electrons from the AAIs to Fe atom. Molecular dynamics simulations studies showed that the AAIs adsorbed the Fe (110) surface in a near flat orientation and the trends of the predicted interaction and binding energies of the equilibrium configurations are in good agreement with the order of experimental inhibition efficiency of the compounds. Both experimental and theoretical studies confirmed that the inhibition performances of the AAIs with cyclic amino substituents (AAI-2 and AAI-3) are higher than that of AAI-1 with an opened-chain

amino group. The inhibition potential was also found to increase with increasing ring size of the cyclic amine and this was attributed to increasing molecular size/volume of the molecule, which corresponds to increase in surface coverage.

4.2. Conclusions

From present investigation embodied in the thesis it is concluded that investigated inhibitors acted as good corrosion inhibitors for mild steel in hydrochloric acid solution and their inhibition performance increases with increasing their concentrations. Results showed that inhibition efficiency of the studied inhibitors increased in presence of electron releasing hydroxyl (-OH) group(s) while presence of electron withdrawing nitro (-NO₂) substituent decreased the inhibition performance. Adsorption of these thirteen corrosion inhibitors over metallic surface obeyed the Langmuir adsorption isotherm. Potentiodynamic polarization study revealed that these inhibitors acted as mixed but predominantly cathodic type inhibitors. Presence of the inhibitors into the acid solution increases the values of R_{ct} and decreases the value of C_{dl} which is attributed due to adsorption of these compounds at metal/electrolyte interfaces. The inhibitive action of the studied compounds was further supported by SEM, EDX and AFM analyses. The quantum chemical calculations and molecular dynamics simulations studies further validated the experimental results.