ABSTRACT

Metals and alloys undergo chemical and/or electrochemical reactions with the environment to form relatively more stable compounds which causes loss of metals and leads to enormous economic losses. 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. The chemical structure, IUPAC name and abbreviation of the thirteen heterocyclic compounds used in the present investigation are given in Table 1. The corrosion inhibition property of the heterocyclic compounds was evaluated using experimental and theoretical methods.

The thesis is divided into four chapters; the first chapter deals with general introduction and critical review on definition, principles, theories, economic impact of corrosion along with technological importance and control measures of corrosion. In the second chapter, the experimental details including synthesis of heterocyclic compounds, methods and materials, sample preparation, chemicals, application of several methods for the evaluation of corrosion inhibition property have been described. The third chapter deals with results and discussion of the experimental and computational data obtained for four series of inhibitors namely, 5-arylpyrimido-[4, 5-b] quinoline-diones (APQDs), 2-amino-4-arylquinoline-3-carbonitriles (AACs), 2, 4-diamino-5-(phenylthio)-5H-chromeno [2, 3-b] pyridine-3-carbonitriles (DHPCs), and 3-amino alkylated indoles (AAIs). Chapter four describes the summary and conclusions of the results obtained from experimental and theoretical means. The thirteen

heterocyclic inhibitors are divided into four sections depending upon the similarities in their structure. The heterocyclic inhibitors in each section are given bellows:

(a) 5-arylpyrimido-[4, 5-b] quinoline-diones (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 (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 (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 (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-arylpyrimido-[4, 5-b] quinoline-diones (APQDs), exhibited high inhibition efficiency and effectively inhibit mild steel corrosion in the acid solution. Results showed that inhibition efficiencies (η%) of the four studied heterocyclic inhibitors at their optimum concentrations (20 mgL^{-1}) obeyed the following order:

APQD-4 (97.82%) > APQD-3 (96.52%) > APQD-2 (95.21%) > APQD-1 (92.17%)

The lowest inhibition efficiency of the APQD-1 is attributed due to presence of electron withdrawing nitrophenyl group at position 5 of the pyrimido-quinolinedione ring. Conversely, the high performances of the APQD-3 and APQD-4 is attributed due to the presence of electron releasing effect of the hydroxyl phenyl group(s) at position 5 of the pyrimido-quinoline-dione ring.

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

AAC-3 (96.52%) > AAC-2 (95.65%) > 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 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:

DHPC-3 (96.69%) > DHPC-2 (96.60%) > DHPC-1 (95.30%)

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

AAI-3 (96.95%) > AAI-2 (96.08%) > AAI-1 (94.34%)

The inhibition efficiency of 3-amino alkylated indoles (AAIs) increases on introducing the ring in the inhibitor molecule as well as on increasing the ring size (or decreasing the ring strain).

Besides the influence of electron withdrawing (-NO_2) and electron releasing (-OH) substituents and ring size of inhibitor molecules, the effect of inhibitor concentration, solution temperature on inhibition efficiency of these heterocyclic inhibitors have been also studied. The results are summarized below:

(i) The inhibition efficiency of all studied inhibitors increases with increasing their concentrations. The maximum inhibition efficiency for best inhibitors from each series of compounds is given as:

- 5-arylpyrimido-[4, 5-b] quinoline-diones; 97.82% for APQD-4 at 20 mgL^{-1}
- 2-amino-4-arylquinoline-3-carbonitriles; 96.52% for AAC-3 at 40 mgL^{-1}
- 2, 4-diamino-5-(phenylthio)-5H-chromeno [2, 3-b] pyridine-3-carbonitriles; 96.69% for DHPC-3 at 50 mgL-1 (12.70 x 10^{-5} $molL^{-1}$)
- 3-amino alkylated indoles; 96.95% for AAI-3 at 250 mgL^{-1} (0.862 mM)

(ii) The inhibition performance all studied inhibitor molecules decreases with increasing solution temperature.

(iii) Among the tested adsorption isotherms, best fit was obtained for Langmuir adsorption isotherm with value of regression coefficient (R^2) close to one.

(iv) The negative sign of ΔG°_{ads} for all studied inhibitors ranging from -33.89 to 37.61 $kJmol^{-1}$ suggest that adsorption of these inhibitors on metallic surface is spontaneous.

(v) The higher values of E_a in presence of all studied inhibitors suggested creation of energy barrier, which in turn reduces mild steel dissolution

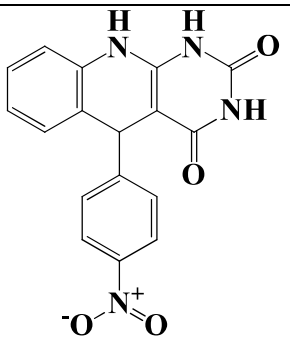
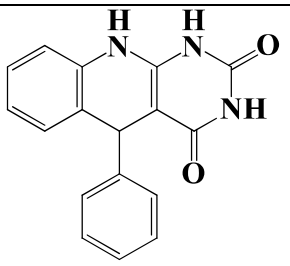
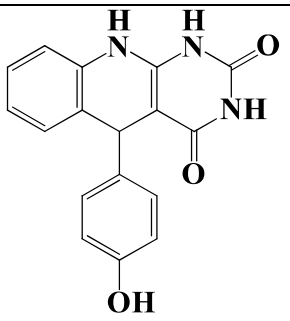
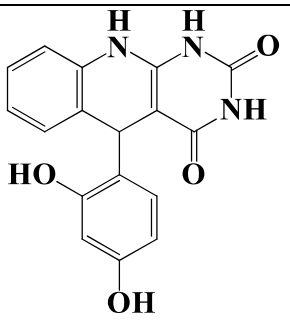
(vi) Potentiodynamic polarization study revealed that all investigated inhibitor molecules act as mixed type inhibitors and behaved predominantly as cathodic one.

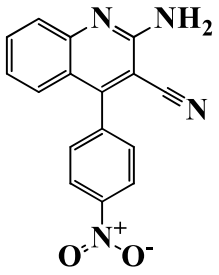
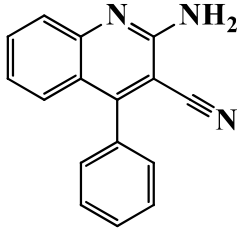
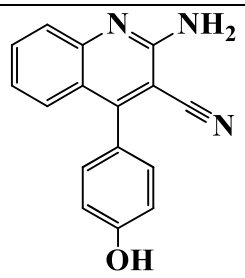
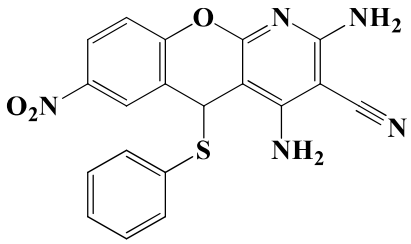
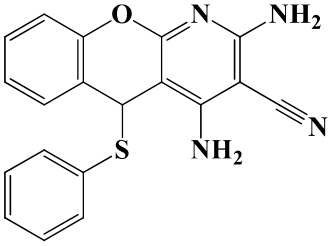
(vii) The increased values of R_{ct} and decreased values of C_{dl} in presence of inhibitors signify these inhibitor molecules acted by adsorption mechanism.

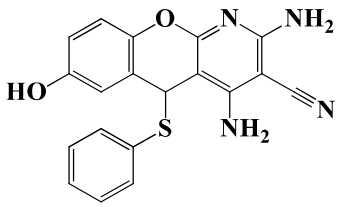
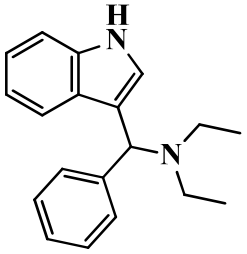
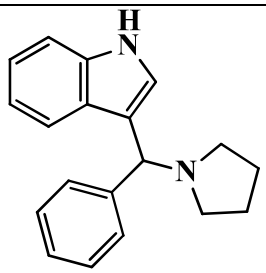
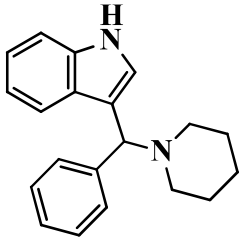
(viii) The surface morphological studies of mild steel specimens using SEM, EXD and AFM techniques suggested that these inhibitor molecules inhibit mild steel corrosion in acid solution by adsorbing on the metallic surface.

(ix) The quantum chemical calculations, using the DFT method on the studied inhibitors was carried out to elucidate their reactivity and selectivity. The Fukui functions suggest the electrophilic and nucleophilic centers in the inhibitor molecules. The values of adsorption energy ($E_{adsorption}$) energies were calculated from molecular dynamics simulations method. A higher value of ($E_{adsorption}$) energies suggests strong interaction between metal and inhibitors.

Table 1: Name and molecular structure of inhibitors studied

S.No.	IUPAC name of Inhibitor	chemical Structure	Abbreviation
1	5-(4-nitrophenyl)-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione		**APQD-1**
2	5-phenyl-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione		**APQD-2**
3	5-(4-hydroxyphenyl)-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione		. **APQD-3**
4	5-(2,4-dihydroxyphenyl)-5,10-dihydropyrimido[4,5-b]quinoline-2,4(1H,3H)-dione		**APQD-4**

5	2-amino-4-(4-nitrophenyl) quinoline-3-carbonitrile		**AAC-1**
6	2-amino-4-phenylquinoline-3-carbonitrile		**AAC-2**
7	2-amino-4-(4-hydroxyphenyl) quinoline-3-carbonitrile		**AAC-3**
8	2,4-diamino-7-nitro-5-(phenylthio)-5Hchromeno[2,3-b]pyridine-3-carbonitrile		**DHPC-1**
9	2, 4-diamino-5-(phenylthio)-5H-chromeno [2, 3-b] pyridine-3-carbonitrile		**DHPC-2**

10	2,4-diamino-7-hydroxy-5-(phenylthio)-5H-chromeno[2,3-b]pyridine-3-carbonitrile		**DHPC-3**
11	N-((1H-indol-3-yl)(phenyl)methyl)-N-ethylethanamine		**AAI-1**
12	3-(phenyl(pyrrolidin-1-yl)methyl)-1H-indole		**AAI-2**
13	3-(phenyl(piperidin-1-yl)methyl)-1H-indole		**AAI-3**