

# CHAPTER 5

## *SUMMARY AND CONCLUSIONS.*

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**Summary and Conclusions**

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**5.1. Summary.**

The current thesis is largely concerned with the corrosion inhibition of N-80 steel in 15% hydrochloric acid solution by eleven organic compounds, including heteroatoms such as nitrogen, oxygen, and sulphur. The corrosion inhibitory capability of these compounds was evaluated using weight loss, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), atomic force microscopy (AFM), quantum chemical calculations, and molecular dynamics techniques.

The thesis is divided into four chapters; the first chapter deals with a general introduction to the definition, principles, theories, and the economic impact of corrosion. This section also deals with the different corrosion control methods and their pros and cons. Chapter two deals with a literature survey on corrosion inhibitors. In chapter; 3, the experimental details, including synthesis of heterocyclic inhibitors, methods and materials, sample preparation, chemicals, and application of several methods for the evaluation of corrosion inhibition properties, have been described. The fourth chapter deals with results and discussion of the experimental and theoretical study data obtained for four series of inhibitors, namely,

1 Triazine-based heterocyclic compounds as corrosion inhibitors

2 Chromeno Naphthyridines as Cls.

3 Quinolines as Cis.

4 Benzimidazoles as Cis.

Chapter five describes the conclusions of the results obtained from experimental and theoretical means. The ten studied corrosion inhibitors are divided into four sections depending upon the similarities in their structure. The Heterocyclic compounds in each section are given bellows:

**(a) Substituted Triazine based HCs as CIs**

- (1) 1,3,5-triphenyl-1,3,5-triazinane (TZ-1)
- (2) 1,3,5-tris(4-nitrophenyl)-1,3,5-triazinane (TZ-2)
- (3) 1,3,5-tris(4-methoxyphenyl)-1,3,5-triazine (TZ-3)

**(b) Chromeno Naphthyridiens as Cis**

- (1) 5-amino-9-hydroxy-2-phenyl-1,11b dihydrochromeno (4,3,2-de) (1,6 naphthtyridine) 4-carbonitrile (CN-1)
- (2) 5-amino- 9-hydroxy-2-(4methoxy phenyl) 1-11b dihydrochromeno (4,3,2 -de) (1,6 naphthtyridine) 4-carbonitrile (CN-2)
- (3) 5-amino- 9-hydroxy-2-styryl 1-11b dihydro 7-oxa 3,6 diazabeno (de) anthracene 4-carbonitrile (CN-3)

**(c) Quinolines derivatives as CIs**

1. 2-amino-7-hydroxy-4-phenyl-1,4-dihydroquinoline-3-carbonitrile (AHQ-1)
2. 2-amino-7-hydroxy-4(4methoxyphenyl)1,4-dihydroquinoline-3-carbonitrile (AHQ-2)
3. 2-amino-7-hydroxy-4(4Styryl)1,4-dihydroquinoline-3-carbonitrile (AHQ-3)

**(d) Benzimidazoles as Cis**

(1) 2-styryl-*1H*-benzimidazole - (STBim)

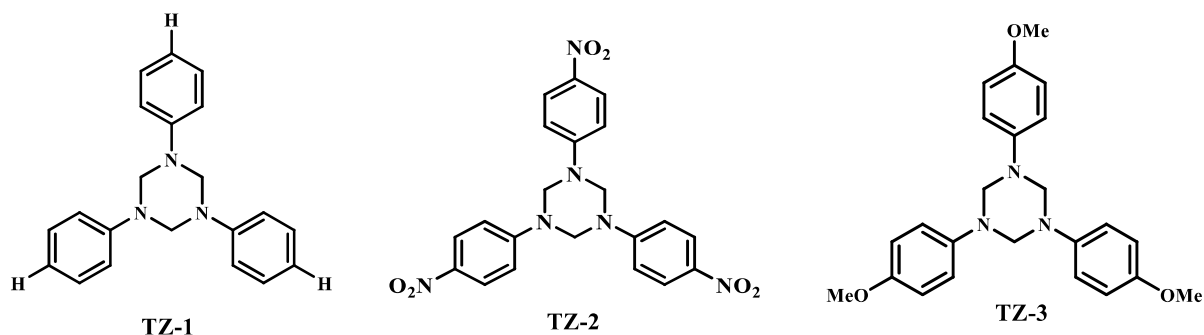
**5.1.1 Substituted Triazines (TZs) as Corrosion Inhibitors**

The inhibition efficiencies of three studied TZs at their optimum concentration of 800 ppm followed the following order:

TZ-3 (93.20%) > TZ-1 (90.60%) > TZ-2 (86.10%)

The highest inhibition efficiency of the TZ3 among the studied inhibitors is attributed to the presence of lone pair of electrons conjugation; due to the Anisaldehyde moiety, which facilitates the adsorption of the inhibitor on the steel surface. The studied inhibitors significantly elevate the activation energy associated with corrosion reaction, thereby reducing the reaction rate. The inhibitor adsorption followed the Langmuir isotherm and showed a high value of the  $\Delta G_{\text{ads}}^0$  supporting chemical adsorption. The inhibition efficacy increased with increasing temperature, indicating that the three inhibitors adsorb well. A polarization study revealed that the compounds under research are mixed type inhibitors with cathodic inhibitive potential. According to an EIS experiment, the presence of inhibitors raises charge transfer resistance ( $R_{\text{ct}}$ ) values due to inhibitor adsorption at metal/electrolyte interfaces. The pKa research demonstrated that the inhibitor compounds have a significant tendency to protonate at the pyridine nitrogen atom at the experimental pH range. The above data, as well as the trend in inhibitory efficiency in the order TZ-3 > TZ-1 > TZ-2, were validated by DFT-based quantum chemical parameters. According to Monte Carlo

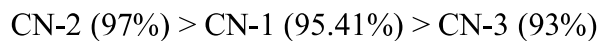
simulations, the protonated TZ-3 has a greater adsorption energy than the neutral molecule, indicating that the inhibitor's primary activity occurs in the protonated form.



**Figure 5.1** Structures of substituted Triazine inhibitors.

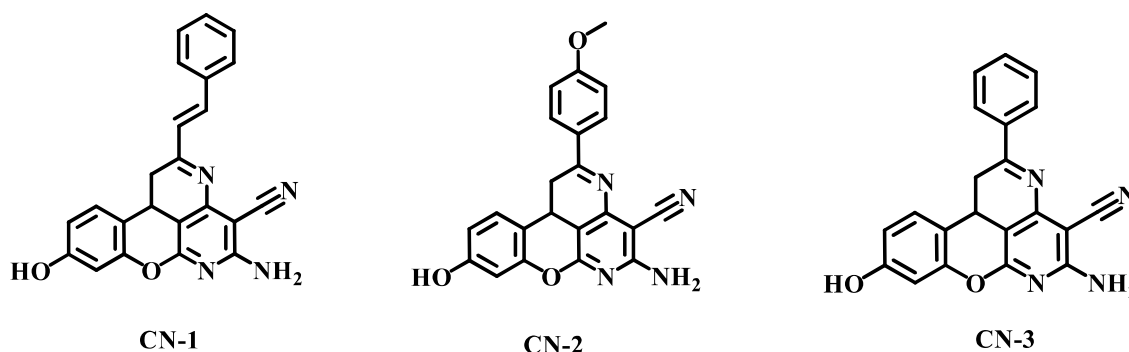
### 5.1.2 Chromeno Naphthyridines (CNs) as Corrosion Inhibitors

The inhibition efficiencies of three studied CNs at their optimum concentration of 500 ppm followed the following order:



The maximum inhibitory efficiency of the CN2 among the examined inhibitors is attributable to the existence of lone pair electron conjugation; due to the anisaldehyde moiety, which enhances inhibitor adsorption on the steel surface. The inhibitors investigated considerably increased the activation energy associated with the corrosion reaction, lowering the reaction rate. The inhibitor adsorption followed the Langmuir isotherm and had a high value of supporting chemical adsorption. The inhibition efficacy increased with increasing temperature, suggesting the three inhibitors' robust adsorption. A polarization investigation demonstrated that the investigated chemicals are mixed type inhibitors with a cathodic

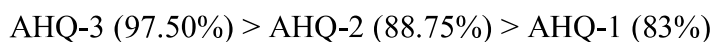
inhibitive capacity. The presence of inhibitors increases charge transfer resistance ( $R_{ct}$ ) values due to inhibitor adsorption at metal/electrolyte interfaces, according to an EIS investigation. The pKa research demonstrated that the inhibitor compounds have a strong proclivity to protonate at the pyridine nitrogen atom at the experimental pH range. The DFT-based quantum chemical parameters confirmed the earlier data and trend in inhibitory efficiency- in the order CN-2 > CN-1 > CN-3. Monte Carlo simulations found that the protonated CN-2 had higher adsorption energy than the neutral molecule, suggesting the inhibitor's principal action in the protonated form.



**Figure 5.2** Structure of Chromeno Naphthyridines

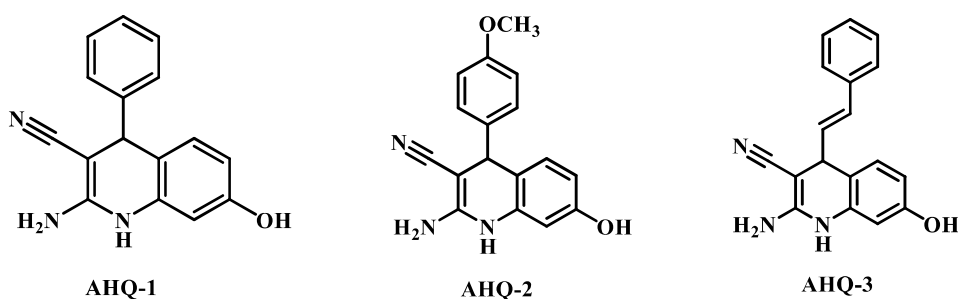
### 5.1.3 Quinolines (AHQs) as Corrosion Inhibitors

The inhibition efficiencies of three studied AHQs at their optimum concentration of 500 ppm followed the following order:



The best inhibitory efficiency of the AHQ3 inhibitor among the tested inhibitors is ascribed to the existence of bond conjugation; due to the cinnamaldehyde moiety, which enhances the inhibitor's adsorption on the steel surface. The inhibitors investigated considerably increased

the activation energy associated with the corrosion reaction, lowering the reaction rate. The inhibitor adsorption followed the Langmuir isotherm and had a high value of supporting chemical adsorption. The inhibition efficiency increased with increasing temperature, confirming the three inhibitors' significant adsorption. A polarization research demonstrated that the investigated chemicals are mixed type inhibitors with mostly cathodic inhibitive ability. EIS analysis demonstrated that the presence of inhibitors increases charge transfer resistance ( $R_{ct}$ ) values due to inhibitor adsorption at metal/electrolyte interfaces. The pKa study revealed that the inhibitor molecules have a considerable tendency to protonate at the pyridine nitrogen atom at the observed pH range. The DFT-based quantum chemical parameters corroborated the preceding data and the trend in inhibitory efficiency in the order AHQ-3 > AHQ-2 > AHQ-1. Monte Carlo simulations demonstrated that the protonated AHQ-3 had higher adsorption energy than the neutral molecule, suggesting the inhibitor's principal action in the protonated form.

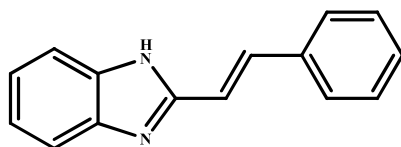


**Figure 5.3** Structures of Quinoline derivative

#### 5.1.4 Benzimidazole based corrosion inhibitors

Cinnamaldehyde was reacted with o-phenylenediamine in a facile synthesis procedure to afford a novel corrosion inhibitor (E)-2-styryl-1H-benzo[d]imidazole (STBim). The

synthesized molecule was completely studied using spectroscopic techniques and employed as an inhibitor for corrosion of Carbon steel (N80 and mild steel) in a 15% HCl environment imitating the conditions of oil-well acidizing. This report contains a thorough examination of the weight loss strategy, electroanalytical tests, and surface analysis. The inhibitor had a high effectiveness of 98% at an optimum dosage of 200 mgL<sup>-1</sup>. The inhibitor adsorption on the steel surface followed the Langmuir isotherm, with inhibition efficiency rising with increasing inhibitor concentration. Impedance measurements revealed that the capacitive performance improved in the presence of the inhibitor. The inhibitor exhibited mixed type behaviour, pushing the corrosion potentials towards the negative direction, indicating a cathodic preponderance of the inhibitor behaviour, as reported in the PDP experiments. Computational analyses using DFT demonstrated that the inhibitor was primarily adsorbed on the steel surface in the protonated form.



**Figure 5.4** Structure of Imidazole derivative

## **5.2. Conclusions.**

The current study, as reflected in the thesis, concludes that the examined inhibitors acted as effective corrosion inhibitors for N-80 steel and Mild steel in hydrochloric acid solution. Their inhibitory performance improves as their concentrations rise. In each series

investigated, AHQ-3, CN-2, TZ-3, and STBim demonstrated the highest inhibitory efficiency at optimum concentration, with STBim showing the highest efficiency (98%). The presence of electron-releasing group(s) and  $\pi$  bond conjugation boosted the inhibition efficacy of the examined inhibitors, while the presence of electron-withdrawing substituent decreased the inhibition performance. The adsorption of these eleven corrosion inhibitors on metallic surfaces followed the Langmuir adsorption isotherm. A potentiodynamic polarization research demonstrated that these inhibitors operated as mixed but primarily cathodic type inhibitors. The presence of inhibitors in the acid solution raises  $R_{ct}$  while decreasing  $C_{dl}$ , which is due to the adsorption of these compounds at metal/electrolyte interfaces. SEM, EDX, and AFM investigations confirmed the inhibitory activity of the investigated substances. The experimental results were well corroborated by quantum chemistry calculations and molecular dynamics simulations.

### 5.3. Scope for Future Work

1. These organic compounds were good corrosion inhibitors. Therefore, these compounds may be tried for other metals in acid solution.
2. The in-situ analysis may be carried out in the presence of these inhibitors.
3. The combination of inhibitors may be tried for the studied metal and other metals or alloys in another acid medium.
4. The corrosion measurements may be tried with various inhibitors above 65°C.
5. The surface study may be done using XPS, etc., to confirm the corrosion product type

# References

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# List of Publications

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List Of Publications and Conferences

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**List of Publications.**

1. **Mohammad Salman**, K.R. Ansari b, Vandana Srivastava a, Dheeraj Singh Chauhan, Jiyaul Haque, M.A. Quraishi, Chromeno naphthyridines based heterocyclic compounds as novel acidizing corrosion inhibitors: Experimental, surface and computational study, *Journal of Molecular Liquids* 322 (2021) 114825.
2. **Vandana Srivastava**, **Mohammad Salman**, Dheeraj Singh Chauhan, Safwat Abdel-Azeimc, M.A. Quraishi (E)-2-styryl-1H-benzo[d]imidazole as novel green corrosion inhibitor for carbon steel: Experimental and computational approach, *Journal of Molecular Liquids* 324 (2021) 115010.
3. **Mohammad Salman**, Vandana Srivastava, M. A. Quraishi, Dheeraj Singh Chauhan, K. R. Ansari, and Jiyaul Haque, Quinoline Carbonitriles as Novel Inhibitors for N80 Steel Corrosion in Oil-Well Acidizing: Experimental and Computational Insights, *Russian Journal of Electrochemistry*, 57, (2021), 3,228–244.
4. **Mohammad Salman**, Kashif R. Ansari, Jiyaul Haque, Vandana Srivastava, Mumtaz A. Quraishi, Mohammad A. J. Mazumder, Ultrasound-assisted synthesis of substituted triazines and their corrosion inhibition behavior on N80steel/acid interface, *Journal of Heterocyclic Chemistry* (2020) 57 (5), 2157-2172.
5. Moses M. Solomon, Saviour A. Umoren, Mumtaz A. Quraishi, **Mohammad Salman**, Myristic acid based imidazoline derivative as effective corrosion inhibitor for steel in 15% HCl medium *Journal of Colloid and Interface Science* 551 (2019) 47–60.
6. D.K. Verma, Fahmida Khan, **Mohammad Salman**, M.A. Quraishi, C.Verma, Inhibition performance of Glycine max, cuscuta reflexia and spirogyra extracts for mild steel dissolution in acidic medium: Density functional theory and experimental studies. *Results in Physics* 10 (2018) 665–674.

7. K.R. Ansari, S. Ramkumar, D.S. Chauhan, **Mohammad Salman**, D. Nalini, V. Srivastava and M.A. Quraishi, Macrocyclic compounds as green corrosion inhibitors for aluminium: electrochemical, surface and quantum chemical studies *International Journal of Corrosion Scale Inhibitor*, (2018), 7, no. 3, 443–459.

### **List of Conferences/Workshops**

1. **Poster presentation** at International Conference **CORCON - 2019**, 23-26 September in Mumbai, (INDIA).
2. **Oral presentation** at International Conference **CORCON - 2021**, 18-21 November in Mumbai, (INDIA).
3. Participation in the five days National **e-Workshop on Instrumentation Techniques in Chemical Sciences (ITCS-2021)**, June 25-29, 2021 (ITCS-2021), June 25-29, 2021 (ITCS-2021), June 25-29, 2021 at Veer Bahadur Singh Purvanchal University.
4. **Poster presentation** at **6<sup>th</sup> national Symposium** on Shaping The Energy Future: Challenges and Opportunities (**SEFCO-2022**) CSIR-Indian Institute of Petroleum, Dehradun, Uttarakhand, India.
5. **Poster presentation** at International conference on Chemical Engineering : Enabling Transition Towards sustainable Future (**ChemTSF – 2022**) 8-10 September 2022, IIT Rurki ,Uttarakhand (INDIA).