# STUDIES OF PLANT EXTRACTS AS ECO-FRIENDLY CORROSION INHIBITORS

JAY PRAKASH RAJAN

DEPARTMENT OF CHEMISTRY

MIZORAM UNIVERSITY

# STUDIES OF PLANT EXTRACTS AS ECO-FRIENDLY CORROSION INHIBITORS

By

JAY PRAKASH RAJAN

DEPARTMENT OF CHEMISTRY

Submitted

in partial fulfillment of the requirement of the Degree of Doctor of Philosophy in Chemistry of Mizoram University, Aizawl.

# MIZORAM UNIVERSITY

(A central University under the Act of Parliament)

Department of Chemistry

School of Physical Sciences

## CERTIFICATE

This is to certify that the thesis entitled "Studies of Plant Extracts as Eco-friendly Corrosion Inhibitors" submitted by Mr. Jay Prakash Rajan, for the degree of Doctor of Philosophy in the Mizoram University, Aizawl, Mizoram, embodies the record of original investigations carried out by him under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the award of the Ph.D. degree. This work has not been submitted for any degree in any other university.

Dated: 30th September, 2019

Raj Kumar Mishra

(Dr. Raj Kumar Mishra)

Co-Supervisor

(Prof. Diwakar Tiwari)

Supervisor

आचार्य दिवाकर तिवारी
Professor Diwakar Tiwari
रसायन विभाग
Department of Chemistry
मिजोरम विश्वविद्यालय
Mizoram University
आइजोल - 796004
Aizawl - 796004

# MIZORAM UNIVERSITY

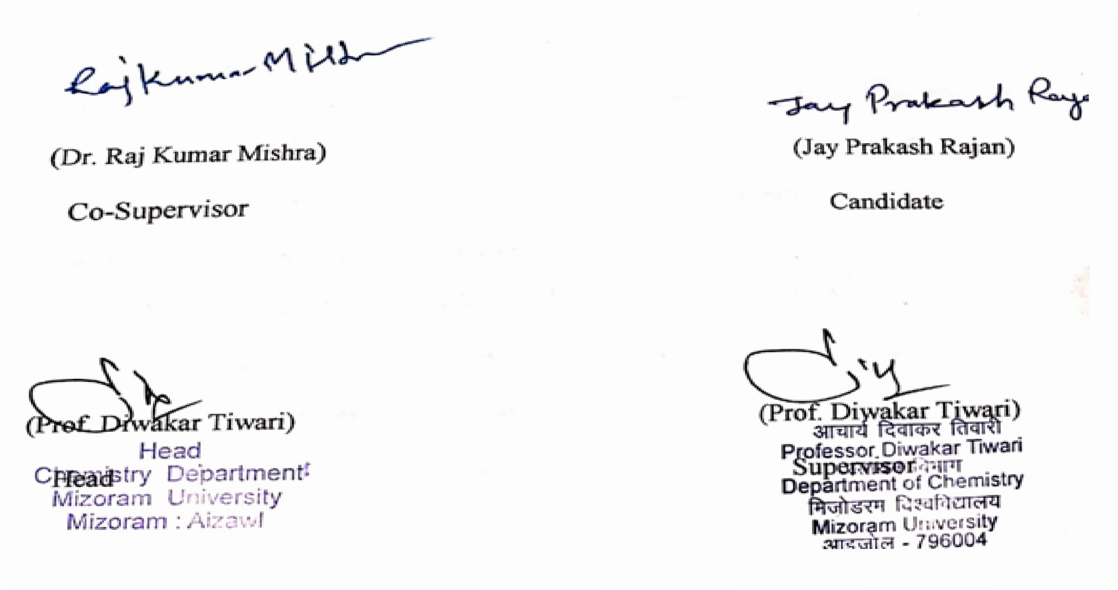
September, 2019

## DECLARATION OF THE CANDIDATE

I, Jay Prakash Rajan, hereby declare that the subject matter of this thesis is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous degree to me or to do the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University/Institute.

This is being submitted to the Mizoram University for the degree of Doctor of Philosophy in Chemistry.

Dated: 30th September, 2019



Rajkumar Mishra

(Dr. Raj Kumar Mishra)

Co-Supervisor

Jay Prakash Rajan

(Jay Prakash Rajan)

Candidate

(Prof. Diwakar Tiwari)

Head

Head
Chemistry Department
Mizoram University
Mizoram : Aizawl

(Prof. Diwakar Tiwari)

Supervisor

आचार्य दिवाकर तिवारी
Professor Diwakar Tiwari
Department of Chemistry
मिजोरम विश्वविद्यालय
Mizoram University
आइजोल - 796004

# ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my research supervisor, Prof. Diwakar Tiwari, and Dr. Raj Kumar Mishra, Department of Chemistry, Mizoram University, for allowing me to carry out my Ph.D. activities, academic, moral support and amazing perspicacity throughout my scientific research; improve my knowledge as well as my research skill.

I would also like to submit my humble gratitude to the present Deans, Prof. Zaithanzauva Pachuau, School of Physical Sciences, Mizoram University for their constructive support and encouragements and inspiration in accomplishing the research work.

I express my heartfelt thanks to the Principal, Pachhunga University College, Dr.Tawnenga for his support and for allowing me to pursue my research program at Mizoram University.

I wish to thank for invaluable input, advice, great support and shared knowledge from Dr.(Mrs.) Grace Skariah, Head, Department of Chemistry, Pachhunga University College; Dr. Raghvendu Pathak, Dr. Thanhmingliana, Dr. C. Lalhriatpuia, Dr. K. Vanlaldinpuia and Dr.Chanambam Victory Devi; along with non-teaching staff, viz., Mr. C. Thansanga, Mr. Lalsawikima and Mr. Ramdinthara, Department of Chemistry, Pachhunga University College.

My sincere thanks to all other faculty members of the Department, viz., Dr. Zodinpuia Pachuau, Dr. N. Mohandas Singh and Dr. Ved Prakash Singh, for their encouragement and support. I thank to all the non-teaching staff of the Department of Chemistry, Mizoram University, for their valuable help and cooperation.

I will remain thankful to my labmate R. Lalneihpuii, Mr. C. Lalnuntluanga and Miss Lalrintluangi for their help in my research work and encouraging during my difficult times, sharing happy moments and many more in Lab research at Mizoram University. I also thank Mr. Brojen Singh, Sr. Laboratory Technician, Department of chemistry, Mizoram University for his continuous help in my research work.

Last but not the least, my deepest gratitude to my parents, my wife and daughter for their support and endless love, constant support and help during my entire work. I have no words to thank Almighty God for everything he has given to me.

(JAY PRAKASH RAJAN)

Regd. No.: MZU/Ph.D/558 of 20.05.2013

## Table of Contents

Pages

Cover page title of thesis I

Inner cover page title of thesis II

Certificate III

Declaration of the Candidate IV

Acknowledgements V

Table of contents VII

List of Figures XII

List of Tables XVII

List of Abbreviation XX

CHAPTER-1

1. INTRODUTION

1.1. Factor influencing corrosion 1

1.2. Classifications of corrosion 3

1.3. Inhibitors 4

1.4. Mechanism and thermodynamics of inhibition process 5

1.5. Economic losses and hazards 7

1.6. Review of literature 8

1.7. Scope of study 17

1.7.1. Importance of acid in industrial process 17

1.7.2. Sustainability and corrosion inhibition 18

1.8. Properties of corrosion inhibitors 19

1.9. Green inhibitors 19

1.10. Outline of present work 19

1.11.1. Allium hookeri 23

1.11.2. Clerodendrum colebrookianum 24

1.11.3. Elsholtzia communis 24

1.11.4. Melocanna baccifera 25

1.11.5. Spilanthes acmella 25

## CHAPTER-2

## 2. METHODOLOGY

2.1. Material 27

2.1.1. Inhibitor 27

2.1.2. Solvent 29

2.1.3. Gas Chromatography- Mass Spectrometry 29

2.2. Methods 31

2.2.1. Material preparation 31

2.2.2. Measurement of corrosion rates 32

2.2.3. Gravimetric measurements 32

2.2.3.1. Adsorption isotherm 33

2.2.3.2. Temperature effect 34

2.2.4. Electrochemical measurements 35

2.2.4.1. Potentiodynamic polarization measurements 36

2.2.4.2. Electrochemical impedance spectroscopy (EIS) 37

2.2.5. Fourier transform infrared (FTIR) spectroscopy and scanning electron microscope (SEM) . 38

## CHAPTER-3

## 3.RESULTS AND DISCUSSION

3.1. Selection of corrosive chemicals 39

3.2. Extract of Allium hookeri (AH) 39

3.2.1. Phytochemical analysis of AH extract by GC-MS 39
3.2.2. Gravimetric measurements of AH extract 42
3.2.2.1. Effect of AH concentration 42
3.2.2.2. Effect of temperature 43
3.2.2.3. Adsorption isotherm 44
3.2.3. Electrochemical measurements of AH extract 48
3.2.3.1. Measurement of potentiodynamic polarization of AH extract 48
3.2.3.2. EIS of AH extract 51
3.2.4. FTIR of MS and AH extract 54
3.2.5. SEM of MS surface 55
3.2.6. Mechanism of corrosion inhibition of AH extract 58
3.3. Extract of Clerodendrum colebrookianum walp Leaves (CCWL) 58
3.3.1. Phytochemical analysis of CCWL extract by GC-MS 58
3.3.2. Gravimetric measurements of CCWL extract 60
3.3.2.1. Effect of CCWL concentration 60
3.3.2.2. Effect of temperature of CCWL extract 62
3.3.2.3. Adsorption isotherm of CCWL Extract 63
3.3.3. Electrochemical measurements of CCWL extract 65
3.3.3.1. Measurement of potentiodynamic polarization of CCWL extract 65
3.3.3.2. EIS of CCWL extract 68
3.3.4. FTIR of MS and CCWL extract 69
3.3.5. SEM of MS Surface 70
3.3.6. Mechanism of corrosion inhibition of CCWL extract 73
3.4. Extract of Elsholtzia communis inflouroscence (ECI) 74
3.4.1. Phytochemical analysis of ECI extract by GC-MS 74
3.4.2. Gravimetric measurements of ECI extract 76
3.4.2.1. Effect of ECI extract concentration 76
3.4.2.2. Effect of temperature 76
3.4.2.3. Adsorption isotherm of ECI extract 77
3.4.3. Electrochemical measurements of ECI extract 82
3.4.3.1. Measurement of potentiodynamic polarization of ECI extract 82

3.4.3.2. EIS of ECI extract 85
3.4.4. FTIR of MS and ECI extract 87
3.4.5. SEM of MS surface 88
3.4.6. Mechanism of corrosion inhibition of ECI extract 91
3.5. Extract of Melocanna baccifera leaves (MBL) 91
3.5.1. Phytochemical analysis of MBL extract by GC-MS 91
3.5.2. Gravimetric measurements of MBL extract 94
3.5.3. Electrochemical measurements of MBL extract 96
3.5.3.1. Measurement of potentiodynamic polarization 96
3.5.3.2. EIS of MBL extract 99
3.5.4. FTIR of MS and MBL extract 100
3.5.5. SEM of MS surface 101
3.6. Extract of Spilanthes acmella (SA) 102
3.6.1. Phytochemical analysis of SA extract by GC-MS 102
3.6.2. Gravimetric measurements of SA extract 105
3.6.2.1. Effect of SA concentration 105
3.6.2.2. Effect of temperature 106
3.6.2.3. Adsorption isotherm of SA extract 108
3.6.3. Electrochemical measurements of SA extract 111
3.6.3.1. Measurement of potentiodynamic polarization of SA extract 111
3.6.3.2. EIS of SA extract 113
3.6.4. FTIR of MS and SA extract 116
3.6.5. SEM of MS Surface 117
3.6.6. Mechanism of corrosion inhibition of SA extract 119

CHAPTER-4

4. SUMMARY AND CONCLUSIONS

4.1. Corrosion Inhibition Studies using Allium hookeri (AH) Extract 120

4.2. Corrosion Inhibition Studies using Clerodendrum colebrookianum (CCWL) Extract 122

4.3. Corrosion Inhibition Studies using Elsholtzia communis (ECI) Extract 124

4.4. Corrosion Inhibition Studies using Melocanna baccifera (MBL) extract 126

4.5. Corrosion Inhibition Studies using Spilanthes acmella (SA) extract 127

4.6. Future Work 129

5. References 131

6. List of publications 165

7. Appendix: Candidate details, published journals papers and biodata

# List of Figures

Figure Page No.

1.1. Classification of corrosion inhibitor. 4

1.2. A schematic representation of the double layer at the interface between an electrode and the electrolyte. 6

1.3. Plant based material for corrosion inhibition process for metal in corrosive medium. 19

1.4. Allium hookeri. 23

1.5. Clerodendrum colebrookianum walp. 24

1.6. Elsholtzia communis (a) leaves (b) inflorescence. 24

1.7. Melocanna baccifera. 25

1.8. Spilanthes acmella. 26

3.2.1. Main phytochemical constituents in AH extract. 40

3.2.2: Variation of corrosion rate with presence of different concentration of AH extract in 1 N HCl at 300K. 42

3.2.3: Variation of corrosion inhibition efficiency with temperature for 0.5 g/L of AH in 1 N HCl. 44

3.2.4: Langmuir adsorption isotherm for AH extract in 1 N HCl. 46

3.2.5: Arrhenius plot for MS in 1 N HCl with and without AH extract. 48

3.2.6: Transition state plot for MS in 1 N HCl containing different concentration of AH extracts. 48

3.2.7: Tafel polarization curves for MS in 1N HCl in absence and presence of various concentrations AH extract. 49

3.2.8: Nyquist plots for MS in 1 N HCl in presence and absence of different concentrations of AH extract. 52

3.2.9: FT-IR spectra of (a) pure AH extract and (b) protective layer of MS after immersion for 3 h in acidic solution with 0.5 g/L of AH extract. 55

3.2.10: SEM image of MS specimen (a) before immersion in acid (b) after 3 h immersion without inhibitor (c) after 3 h immersion with the 0.5 g/L of AH. 57

3.2.11: Schematic illustration of different modes of adsorption of AH extract on metal/acid interface. 58

3.3.1: Main phytochemical constituents in CCWL. 60

3.3.2: Variation of corrosion rate with different concentration of CCWL extract. 62

3.3.3: Variation of corrosion rate of MS at different temperatures in presence of 0.4 g/L concentration CCWL extract. 62

3.3.4: Langmuir adsorption isotherm in presence of CCWL extract for MS in 1 N HCl. 63

3.3.5: Arrhenius plots for MS corrosion rate versus 1/T in 1 N HCl presence and absence of CCWL extracts. 64

3.3.6: Transition-state plots for MS corrosion rates in 1 N HCl in absence and presence of various concentrations of CCWL extracts. 65

3.3.7: Polarisation curves for MS in 1N HCl in absence and presence of different concentrations of CCWL extract at 303K. 67

3.3.8: Nyquist plot for MS in acidic solution in absence and presence of 68 various concentration of CCWL extract.

3.3.9: FT-IR spectra of (CC) pure CCWL extract and (FE-CC) protective layer developed on MS after immersion in 1 N HCl containing 0.4 g/L of CCWL extracts for 3h. 70

3.3.10: SEM images of MS: (a) before immersion in corrosive solution; b) after immersion in 1 N HCl for 3 h and (c) after immersion in 1N HCl solution containing 0.4g/L of CCWL extract for 3 h. 72

3.3.11: Schematic corrosion inhibition mechanism of main constituents' compounds in crude CCWL extract. 74

3.4.1: Main phytochemical constituents in ECI extract. 74

3.4.2: Variation of corrosion rate with 0.5g/L of ECI extract in 1 N HCl at various temperature. 77

3.4.3: Langmuir adsorption isotherm plots for MS in 1 N HCl solutions in the presence of various concentrations of ECI extract at different temperature. 78

3.4.4: Arrhenius plot for the inhibition of corrosion of MS in1 N HCl without and with different concentrations of ECI extract. 80

3.4.5: Transition state plot for MS corrosion in 1 N HCl at different concentrations of ECI extracts. 82

3.4.6: Tafel polarization curves for MS in 1 N HCl in absence and presence of various concentrations of ECI extract at 300K. 83

3.4.7: Nyquist plots for MS in 1 N HCl without and with different concentrations of ECI extract at 300 K. 85

3.4.8: FTIR spectra of (a) pure ECI extract and (b) protective layer developed on MS after immersion for 3 h in 1 N HCl containing 0.5g/L concentration of ECI extract. 87

3.4.9: SEM images of MS surface topography: (b) before immersion in corrosive solution; (a) after immersion in 1 N HCl for 3 h; (c) after immersion in 1 N HCl solution containing 0.5g/L ECI extract for 3 h. 90

3.4.10: Schematic diagram of mechanism of corrosion inhibition reaction with main constituent of ECI extract on MS. 91

3.5.1: Main phytochemical constituents in MBL extract. 92

3.5.2: Schematic diagram of corrosion inhibition reaction mechanism of MBL extract on MS. 95

3.5.3: Corrosion rates of various concentrations of MBL extract on MS surface in 1 N HCl at 303 K. 96

3.5.4: Tafel polarization curves of MS immersed in 1 N HCl with MBL concentration (a) Blank; (b) 0.1g/L (c) 0.3g/L (d) 0.5g/L. 98

3.5.5: Nyquist plots for MS in 1N HCl without and with different concentrations of MBL extract at 303 K. 99

3.5.6: FTIR spectrum of MBL extract and protective layer formed on metal surface (MBL-Fe) in 1 N HCl solutions. 101

3.5.7: SEM image of MS specimen (a) after 3 h immersion in acidic solution and (b) after 3 h immersion in acidic solution with the 0.5g/L of MBL extract. 102

3.6.1: Structure of main constituent in crude SA extract. 103

3.6.2: Corrosion rate of MS at various concentration of SA extract in 1 N HCl. 106

3.6.3: Variation of corrosion rate at different temperature in the presence of 0.5g/L SA extract. 107

3.6.4: Langmuir adsorption isotherm at 300 K for MS in 1 N HCl with and without various concentrations of SA extract. 108

3.6.5: Arrhenius plots for the corrosion of MS in 1 N HCl solution in the absence and presence of the inhibitor in different concentration of SA. 110

3.6.6: Transition plots for the corrosion of MS in 1 N HCl solution in the absence and presence of the SA extract. 111

3.6.7: Potentiodynamic polarization curves for MS in 1 N HCl solution without and with different concentrations of SA extract at 300 K. 112

3.6.8: Nyquist plots for MS in 1 N HCl solution without and with different concentrations of SA extract at 300 K. 115

3.6.9: FT-IR spectra of (SA-Fe) scratched surface of MS containing 0.5 g/L of SA extract after 3 h. 116

3.6.10: SEM image of MS specimen (a) before immersion in acidic solution (b) after 3 h immersion in acidic solution and (c) after 3 h immersion in acidic solution with the 0.5g/L of SA extract. 118

3.6.11: Schematic diagram of the adsorption process of SA extract MS surface in 1 N HCl. 119

# List of Tables

| Table | Page No. |
|---|---|
| 3.2.1: Chemical constituents present in the AH extract using the GC-MS analysis. | 41 |
| 3.2.2: Weight loss results for MS in 1N HCl in the absence and presence of various concentration of AH extract. | 43 |
| 3.2.3: Free energy and adsorption parameters of MS in 1 N HCl containing different concentration of AH extracts. | 45 |
| 3.2.4: Thermodynamic parameters for MS dissolution in 1 N HCl solution in the absence and presence of various concentration of AH extract. | 47 |
| 3.2.5: Tafel polarization parameters for MS corrosion in 1N HCl in the presence and absence of AH extract. | 50 |
| 3.2.6: Corrosion parameters obtained from Nyquist plot from EIS measurement of MS in 1 N HCl without and with different concentration of AH extract. | 53 |
| 3.3.1: Chemical constituents present in the CCWL extract using the GC-MS analysis. | 59 |
| 3.3.2: Gravimetric analysis for MS in 1 N HCl at 303 K in absence and presence of various concentrations of CCWL extract. | 61 |
| 3.3.3: Thermodynamic parameters for MS in acidic medium in various concentration of CCWL extract at a temperature range (303K - 333K). | 65 |

3.3.4: Electrochemical parameter obtained from low carbon steel in 1N HCl in absence and presence of different concentrations of CCWL extract at 303 K. 67

3.4.1: Chemical constituents present in the ECI extract using the GC-MS analysis. 75

3.4.2: Gravimetric analysis for MS in 1 N HCl at 300 K in absence and presence of various concentrations of ECI extract. 76

3.4.3: Calculated values of adsorption isotherm adsorption and standard free energy for the adsorption of ECI extract on MS surface in 1 N HCl solution at different temperatures. 79

3.4.4: Thermodynamic activation parameters for MS in 1N HCl solution obtained from gravimetric measurements of ECI extract. 81

3.4.5: Tafel polarization parameters obtained for MS in absence and presence of different concentrations of ECI extract in 1 N HCl at 300 K. 84

3.4.6: Impedance parameters for MS in 1 N HCl in absence and presence of different concentrations of ECI extract at 300 K. 86

3.5.1: Chemical constituents present in the MBL extract using GC-MS analysis. 93

3.5.2: Corrosion rate and surface coverage by weight loss in absence and presence of MBL extract for 5 h. 94

3.5.3: Corrosion parameters obtained from potentiodynamic polarization for MS in 1N HCl solution in the absence and presence of different 98 concentrations of the MBL extract at 303 K.

3.5.4: Impedance parameters for MS in 1 N HCl solution in the absence and in the presence of different concentrations of MBL extract. 100

3.6.1: Chemical constituents present in SA extract using the GC-MS analysis. 104

3.6.2: Corrosion rate and inhibition efficiency at various concentration of SA extract in 1 N HCl at 300 K. 106

3.6.3: Calculated value of adsorption isotherms and respective free energy for the adsorption of SA extract on MS surface in 1 N HCl solution at different temperatures. 109

3.6.4: Arrhenius activation thermodynamic parameters for MS in 1 N HCl in the presence of various concentrations of SA extract. 110

3.6.5: Measurement of electrochemical parameters for the MS in 1 N HCl solution in absence and presence of different concentration of SA extract at 300 K. 113

3.6.6: Impedance parameters for MS in 1 N HCl solution in the absence and in the presence of different concentrations of SA extract. 115

(v) Physical state of metal: The rate of corrosion is influenced on physical state of metal.

(vi) Nature of surface film: Specific volume ratio which is defined as the ratio of volumes of the metal oxides to the metal is inversely proportional to corrosion rates.

(vii) Passive character of metal: Passive metals viz., chromium, cobalt, nickel show higher corrosion resistance.

(viii) Solubility of corrosion products: Solubility of corrosion products in corrosive medium enhances the corrosion rates.

(ix) Volatility of corrosion products: Volatility of corrosion products also enhances the corrosion rates.

B. Nature of environment

(i) Temperature: It is well known that the corrosion is electro-chemical reaction and it will follow an Arrhenius relationship. Therefore, corrosion of metals increases with increase in temperature.

(ii) Presence of moisture: The moisture gets adsorbed on metal surface by different ways. This is possible to capture acidic gas from surroundings on the metal surface. Therefore, it provides conductive path for electrochemical reaction on the metal surface and increases the deterioration of material.

(iii) Effect of pH: Metallic material severely deteriorated by exposure in alkaline or acidic medium. The higher concentration of hydrogen ion or anion directly influences the cathodic and anodic processes by the formation of corrosion products.

## 1.2. Classifications of Corrosion

(i) Uniform corrosion: Uniform corrosion is a form of corrosion where the surface is removed almost evenly. The partial reactions (metal dissolution and oxygen reduction) are statistically distributed over the surface, leading to more or less homogenous dissolution of the metal and uniform formation of corrosion products e.g., red rust on steel.

(ii) Pitting corrosion: Pitting corrosion is a localized form of corrosion that leads to the creation of small holes or “pits” in the metal. This form of corrosion is mainly found on passive metals such as aluminium, titanium and stainless steel. The corrosion initiating process starts with a local break-down of the passive layer. Local corrosive attack can be initiated on stainless steels, for example, by chloride ions.

(iii) Crevice corrosion: Crevice corrosion refers to corrosion occurring in cracks or crevices formed between two surfaces. This type of corrosion is initiated by the restricted entrance of oxygen from the air by diffusion into the crevice area leading to different concentrations of dissolved oxygen in the common electrolyte.

(iv) Stress corrosion cracking: Stress corrosion cracking (SCC) is a combined mechanical and electrochemical corrosion process that results in cracking of certain materials. Internal stresses in a material can be sufficient to initiate an attack of stress corrosion cracking. Initially, a small pit is formed and develops into a crack due to applied or residual stress in the material.

(v) Non-Passive surface: The crack formation due to a new active (non-passive) metal surface, which easily interacts with surrounding environment and start degradation. This leads to new highly active metal surfaces in the crack.

(vi) Galvanic corrosion: Galvanic corrosion refers to corrosion damage when two dissimilar metals are in contact in presence of electrolyte.

## 1.3. Inhibitors

The use of inhibitors is an important method of protecting materials against deterioration due to corrosion attack especially in acidic medium (Trabanelli, 1991). A corrosion inhibitor may be inorganic or organic molecule that, upon addition of corrosive environment, leads in reduction of corrosion rate in an acceptable level. Corrosion inhibitors are generally used in small concentration and must be compatible with a particular corrosive environment.

The inhibitive action of a corrosion inhibitor takes place in two ways i.e. (i) by altering the corrosive environment into noncorrosive or less corrosive environment through its interaction with corrosive species that is environment modifiers and (ii) by interacting with metal surface to form protection layer on adsorption inhibitors. This deals with green corrosion inhibitors. Figure 1.1 is schematic diagram of adsorption inhibitors classification (Sashtri, 2011):

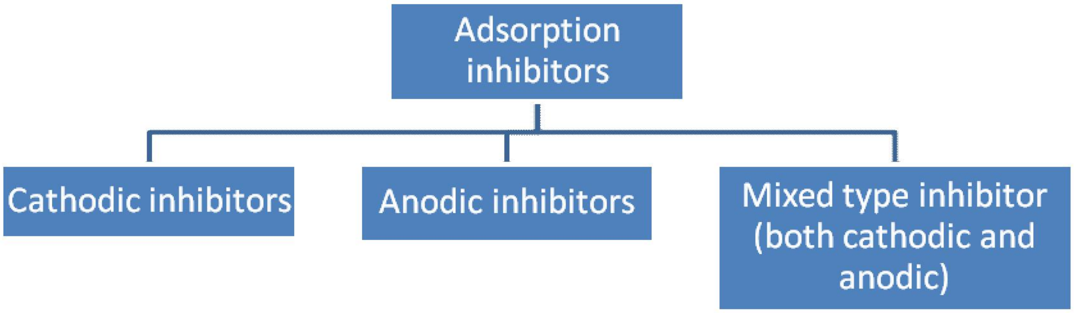


Figure 1.1.: Classification of corrosion inhibitor.

Cathodic inhibitors affect the cathodic side of polarisation curve inhibiting by hydrogen evolution in acidic corrosive environments or by reducing the oxygen of neutral or alkaline corrosive environments. Inorganic phosphates, silicates, or borates in alkaline solutions and carbonate of calcium and magnesium are few examples of cathodic inhibitors. However anodic inhibitors are more effective in neutral or alkaline corrosive environments. Chromates, molybdates, tungsten and sodium nitrite are few examples of anodic inhibitors. Many organic compounds behave as mixed-type inhibitors, which affect both anodic and cathodic branches of polarisation curves. Organic compounds with amino group (-$NH_2$), carboxyl group (-COOH), phosphonate group (-$PO_4$) are known for their mixed type of inhibiting activity.

Uses of many synthetics inorganic and organic inhibitors are now being gradually restricted due to various environment issues. As a result, corrosion scientist and engineers are investigating and designing eco-friendly bio-compatible green corrosion inhibitors in the last two decades (Roy et al., 2014). The extracts of Chamomile, Halfabar, Black cumin and kidney bean were investigated as corrosion inhibitor for steel in corrosion under acid medium (Raja and Sethuraman, 2008). The anticorrosion activity of various plant extracts arereported by different authors, which was reviewed by Raja and Sethuraman (2008).

### 1.4. Mechanism and Thermodynamics of Inhibition Process

The mechanism of the inhibition process of organic inhibitors is mainly due to their adsorption at the metal–solution interface, which is accompanied by a change in potential difference between the metal electrode and the solution. This change in potential difference is due to the non-uniform distribution of electric charges at the metal electrode–solution interface, which is characterized by an electrical double layer, sometimes by a triple layer. A schematic representation of the electrical double layer is given in Figure 1.2 (Christensen et al., 1994; Sastri, 2011).

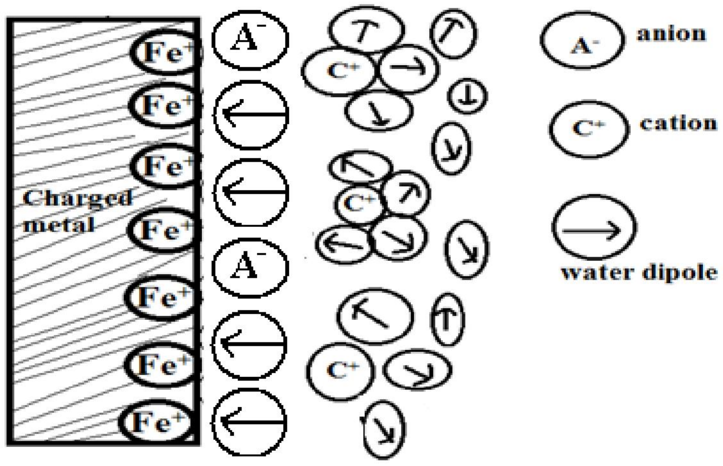


Figure 1.2: A schematic representation of the double layer at the interface between an electrode and the electrolyte.

Cations are normally hydrated due to their small radii as the free energy of salvation is proportional to ratio of cation charge and its ionic radius (Christensen et al., 1994). The plane formed by the nuclei of anions directly adsorbed on the metal surface is termed as the Inner Helmholtz Plane (IHP). The addition of a corrosion inhibitor into the electric double layer changes its composition and structure. Hence, measurement of the capacitance of the double layer before and after the addition of the corrosion inhibitor is used to monitor the adsorption of the inhibitor.

The process of adsorption is governed by different parameters especially by the chemical structure of the organic inhibitors; which in turns are characterized by different spectroscopic techniques such as Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography coupled with Mass Spectroscopy (GC-MS). Adsorption of organic inhibitor molecules onto metal surface is analysed by two possible interactions: physisorption which is favourable in presence of electrically charged metal surface and charged species in the bulk of the electrolytic solution and chemisorption which involves charge-sharing or charge-transfer from the inhibitor molecules to the metal surface to form a coordinate or chemical bond (Deyab, 2014). These adsorption phenomena are also explained on the basis of energy because the interaction energy between organic inhibitor molecule and metal surface is higher than that between water molecule and metal surface. The inhibition effect of organic molecules thus due to their adsorption via available functional group in them onto the metal surface.

It is useful to examine the corrosion process in terms of thermodynamics, which governs the electrochemical basis of corrosion. The values of corrosion rates and the inhibition efficiency are function of thermodynamic parameters like temperature etc. The associated activation energy and the free energy of adsorption are directly linked with corrosion rates and hence important to discuss in detail the corrosion inhibition. These parameters are also used to understand the mechanism of adsorption of inhibitor molecules onto the metal surface (Yadav et al., 2012).

## 1.5. Economic Losses and Hazards

The global cost of corrosion is estimated to be 3.4% of the global gross product (GDP) By using available corrosion control practice only 15-35% of the cost of corrosion is to be saved on a global basis (Koch et al., 2016). According to NACE (National Association of Corrosion Engineers) report maintenance cost due to corrosion is predicted around 5% of the GDP. For India the cost of corrosion is around half of our defence budget and perhaps double of our total annual expenses on education. It is, therefore an enormous sum, which needs immediate attention and future strategy to minimize it and make our industry safer and accident free (Singh et al., 2010).

The Global corrosion inhibitor market is driven by rising demand from metal industries, power generation industries, oil and gas industries. Corrosion is a menace and it is responsible for the loss of billions of dollars every year. As a result, there is significant demand for corrosion inhibitors across the globe. Serious ecological problems such as oil spills, fire accidents and human losses after explosions occurs, due to leakage of corrode metals or alloys which are used for machinery purposes. According to the NACE assessment report, corrosion is considered as the largest contributor to the degradation of valuable industrial machine and historical building (Kochet al., 2002). NACE is corrosion professional society, which promotes public safety, environment protection, and reduction of economic impact of corrosion. For decades, corrosion professionals have made great technologies, employing effective management practices, and increasing public awareness about the critical corrosion control and incorporating the control strategies to save money, environment and human lives (Espallargas, 2015).

## 1.6. Review of Literature

Science and technology are based on the thinking, skill, observations and from the learning subjects. They explore in new ideas for the uses of humanity and meet the needs of human being are fulfilled (Maqbool et al., 2017). Humans have always been curious about nature and innovating new technology. It is skill to canalise some processes and improve the quality of material. Research is always solving a specific problem and our desires are connected to it and push research into a more fruitful direction to benefit the society (Wilbertz, 2013). In the modern society, the increasing importance of material sciences had an important role in the improvement of the quality of material. Exchange of ideas coming out from various researches facilitates the industry progress (Zhou et al., 2008). This tendency arises from the constant and better change in industry, development and modernization of technology.

In order to make the products with the required properties, the materials science and engineering are to be synchronized. The main priorities are the continuous improvement of existing materials, ensuring environment protection and improving conditions as well as extending of material life. Research on material science will have to play a key role in the process of changing industrial society. It should be noted that the research and development are to protect living word from the hazards of nature. The success of research has great impact on existing function and modifies some functions. It creates new options for improvement and increases the performance of the material. It creates a prominent growth in the industry as it facilitates further growth that can be sustained by other options (Mulder, 2007).

Over the last few decades, corrosion inhibition of mild steel has become one of the most important areas due to its direct economic loss as well as environmental contamination (Garcia-Arriaga et al., 2010). It makes serious ecological problems such as oil spills, fire accidents and human losses after explosions due to leakage. The effects of corrosion on our daily lives are directly or indirectly concerted such as corrosion recognized on grills, metal tools and transportation systems (bridge and roads). The corrosion of steel can precede suddenly failure of infrastructure in highway, electrical towers and buildings, collapse of the same result in significant economic loss and death of humans (www.nace.org).

According to literature, Union Carbide India Limited (UCIL) operated machine with far below the standards and plant operators noticed a small leak of Methyl Isocyanate (MIC) gas (Shrivastava, 1987; Carlsten 2003). In 2016, a train derailed near Kanpur due to corroded and weak maintenance of railways track as a result loss of life more than fifty. The government and environmental regulatory bodies are being intended to monitor time to time and give emphasise on the management as well as take preventive measures to avoid such accidents to take place. A proper attention is to be given to deal the corrosion problem for safety as well to reduce risk and environmental pollution. The safety of life due to fracture of structure, tank leakage and poisonous inflammable liquid contaminate the surrounding environments (Bardal, 2004). These examples produce evidence how can corrosion result into extreme catastrophic accident in modern era (Asrar et al., 2016).

Our nation loses around 4-5% of GDP annually on due to corrosion, which affects significantly the economic growth due to damage of Infrastructures, such as bridges, highways, public utility, Airports, Metro Stations, Railways stations etc. Management of corrosion is not only important for the structures, but safety also for the public using these structures daily, and hence the importance of corrosion can no longer be ignored. Our country is going through the phase of urbanization and in the upcoming years, there will be boom with infrastructure. Hence, corrosion management could play a very important role.

The chemical industry has undergone tremendous changes in the past decade. The aspects of energy, environment and health have catalysed to improve in plant construction for reliability and safety performance (Terekhova et al., 2017). However, some of the equipment may develop corrosion product during operational period. The purpose is to clean the metal surface, to produce a homogeneous smooth cover and to provide a contamination free product (Norman et al., 2006)

During chemical process, contamination is deposited in the equipment and enhances the corrosion attack. From the corrosion point of view, these are adhered and deposited and can cause severe corrosion problems. These types of contamination can cause localised corrosion and formation of pin holes in the equipment. The popular approaches to clean the contamination are acidic solutions such as, sulphuric acid ($H_2SO_4$), hydrochloric acid (HCl) and phosphoric acid ($H_3PO_4$). Organic acids such as formic, acetic and citric acid, along with alkaline solutions also used as cleaning agent. These cleaning processes are essentials and unavoidable, however; these processes itself are corrosive and damaging the equipment. Hence, corrosion inhibitors are used with cleaning agent to minimize the corrosion of metallic equipment (Gadiyar et al., 1991).

Rapid urbanisation and growth of industries based on petrochemical process industries can impact of corrosion due to use of crude petrochemicals, which contain inorganic and organic acids, that reduces the life of equipment (Wanklyn, 1982; Papavinasam, 2000; Miksic et al., 2009). Development of numerous vehicles for transportation on the land, sea, and air requires efficient fuel as a result intensive development of oil refining and petrochemical industries. Metallic equipment used in refinery industry comes into contact with corrosive medium such as water, atmosphere and soil. Therefore, it requires managing and monitoring the risks of corrosion and possible accidents. Corrosion is the most threatening factor of damage for important equipment in various industries. The assessment of the corrosion predicted the probable failure that play important role in corrosion management systems and analysis of failure of various important equipment (Naemnezhad et al., 2017). Corrosion of equipment in crude petroleum refineries units is based on surrounding environmental conditions. For example, below 373 K the presence of HCl and $H_2S$ gases or at 473 K in NaCl and $Na_2SO_4$ salts are more aggressive to damage the refinery equipment (Gutzeit et al., 1987; Groysman, 2014).

Corrosive agent such as HCl appears in crude oil as a by-product of hydrolysis of calcium and magnesium. The most corrosive contaminants are removed during preliminary process of crude oils however some contaminants in marine tankers and pipelines are inorganic salts ($CaCl_2$, $MgCl_2$, and NaCl). This is remaining in crude oil even after desalting. These corrosive agents remain in crude oil which passes in distillation column and goes up with light hydrocarbons and cause a major problem in the petroleum refining unit. It can also occur with reforming and hydro treating process units and damage the refinery equipment (Wright, 1987; Lai, 1990; Lewandowski, 2000; Antos, 2004; Groysman, 2010). The organochlorine used in catalytic reformers in petrochemical process (Groysman, 2010) is also found in crude petroleum product. These are corrosive in nature and damage the distillation unit due to HCl formed after hydrolysis of organochlorine. This strong inorganic acid causes corrosion and failure of expensive equipment.

The fertilizer industry is the most important industry for agriculture sector. Variety of raw materials such as water, air, hydrogen sulphide, nitrogen containing compounds, polythionic acids, organic chloride compounds, sulphuric acid, and alkaline solutions (sodium hydroxide, sodium carbonate, ammonium hydroxide, amines, sour water, and spent caustic) are used for the production of various types of fertilisers. Sometimes these compounds are decomposed or react to each other to produce corrosive substances such as ammonia or hydrogen sulphide, di-hydrogen ammonium phosphate or ammonium nitrate, which enhance the corrosion of metallic material. The fertiliser companies also use high concentration of phosphorous, sulphur and chloride containing compounds. Cleaning and sanitation agents such as alkaline, acidic, strong or weak oxidizing and reducing chemical are also employed to remove contaminates to maintain hygiene level. These great varieties of corrosive environments and aggressive chemical agents promote the corrosion of equipment and damage them. Further allergy to metals and its release into the food chain is the greatest health hazard to human and another organism (Valdez, 2004).

In the automobile system, failures are reported due to synergistic effect of mechanical stress and corrosion, such as corrosion fatigue cracking. Usually, the automobile parts are always exposed to corrosion environment such as de-icing salt, aggressive ion, water and oxygen. The life and safety of automobile parts are reduced mainly due to fatigue and corrosion (Kim and Kim, 2017). Materials with good mechanical ability require a good surface finish, and could be uniformly modified through microstructure and adjustment of chemical components (Boothroyd and Knight, 1989; Finn, 1989; Zheng et al., 2013).

Right from beginning of invention iron, it exists with rust which slowly destroys the iron, when it comes in contact with surrounding environment such as oxygen and water (Rao, 2000). In all metals, extraction from ores involves taking energy as a result of this metal becomes thermodynamically unstable and tend to revert back to the thermodynamically stable native oxide state when it is exposed to the surrounding atmosphere.

However, there are many other factors that affect the corrosion of iron, especially the presence of contamination, such as chloride, sulphate, ammonia, organic matter and microorganisms. Corrosion of metal is an electrochemical process and electrolyte, one of the main contributors for the metal corrosion that is involved in the electrochemical corrosion. Aggressiveness of anion depends on the presence of oxygen, concentration of cation, temperature, and pH of solution, which leads to corrosion (Foley, 1970).

The development in science and technology requires variety of metallic materials with good corrosion resistant properties and cost effective. To improve the inhibition efficiency and to minimize the consumption of toxic material, an attempt has been made to incorporate natural materials or composites which are considered to be among the most promising approach to be investigated extensively. In recent years, many studies have been dedicated to utilize natural products such as coconut shell, wood, pineapple leaf and palm kernel shell. Therefore, due to the non-toxic nature, low cost and increasing awareness the use of natural product as corrosion inhibitor is receiving greater attentions.

It has developed different techniques and processes for making mild steel. In the past, steel was produced based on individual knowledge and skill (Prakash, 1983). Ancient Indian iron workers had technological skill to manufacture sharp edged like swords or rust-less Delhi iron pillar, referred to as “rust-less wonder” (Anantraman, 1996). The iron pillar at Delhi is called rust-less since it has withstood without corrosion for the last 1600 years. It has been recorded that Indian steel have been used in construction of the London bridge in England. The famous iron sword of Tipu Sultan is made from corrosion resistant iron. Indian smiths were aware of corrosion process of iron therefore, developed high quality of iron by changing the composition of iron during forging process, which is less susceptible of corrosion (Kumar and Balasubramaniam, 1998; Balasubramaniam, 2000).

In view of the availability, low toxicity, bio-degradability and compatibility, the use of eco-friendly corrosion inhibitorshas received greater attention in recent time. A considerable number of studies have investigated the inhibition effectiveness of plants extracts as good corrosion inhibitors for mild steel in acidic environment. Interestingly, plant extracts contain wide variety of phytochemical constituents, such as polyphenols, amino acids, terpenes, carboxylic acid, pigments resins and alkaloids (Deyab et al., 2017). Most of thesecompounds contained with heteroatom and multiple bonds, which possess the similar electronic structures as conventional organic corrosion inhibitors hence, found to be potential corrosion inhibitors.

Haldhar et al. (2018) tested the corrosion inhibition effectiveness of Valeriana wallichii extract for mild steel in acidic solution. It was reported that plant extract shows good inhibition performance of 93.47% at500 mg/L at 298 K. The phytochemical studies confirmed that the naphthoic acid and iridoid derivative are main active constituents of the Valeriana wallichii extract.Based on polarization measurementssuggested that the inhibitor molecule acts as a mixed type of inhibitor.

The extract of Epimedium was reported to be fairly good anticorrosion for mild steel in 5% HCl solution. It was reported by Singh et al.(2019)that extract of Epimedium inhibit the corrosion reaction and inhibition upto 96.7 % at high temperature 60 °Cusing 1.0 g/L extract.Thermodynamic measurements confirmed that the physical and chemical adsorption mechanism was involved at the metal surface. It was reported that the main phytochemical constituent of Epimedium contained with O and N heteroatoms, which are predominantly coordinate with lone pair of inhibitor molecule and vacant d-orbital of metal surface.

Zheng et al. (2018) investigated the corrosion inhibition performance of Eriobotrya japonica extract for mild steel in $H_2SO_4$ solution. It was reported that the ursolic acid, citric acid and palmitic acids are the main constituents of Eriobotrya japonica extract.The polarization measurements confirmed the inhibitor molecule acted as a cathodic inhibitor. Krishnan et. al. (2018) investigated the corrosion inhibition property of Turbinaria ornata (TO) extract on mild steel in HCl medium. It was confirmed that the octadeconic acid was the main phytochemical component in Turbinaria ornata extract having the efficiency of 100% at 25 g/L. Based on the $CL_{50}$(Toxicology)measurements, it was suggested that the Eriobotrya japonica are 20 times less toxic than other synthetic organic inhibitors.

Similarly, the inhibitive effects of polyaspartic acid derivatives on acid corrosion of mild steel was investigated by Chai et al. (2018). It was reported that polyaspartic acid chemisorbed on metal surface by forming the coordinate bond between the lone pair of inhibitor molecule and vacant d-orbitals of metal.Loto and Loto (2019) evaluated the inhibition effectiveness of Rosmarinus officinalis and trypsin complex for mild steel in $H_2SO_4$ and HCl solutions.Based on the corrosion polarizationstudies the authors suggested that, the extract of Rosmarinus officinalis and trypsin complex in $H_2SO_4$ medium, the inhibitor molecule acted as anodic type of inhibitor and HCl medium it was acted as a cathodic type of inhibitor. The main functional group in phytochemicals are alkenes, aldehydes, nitrile, alkynes, esters, ketones and amines. These components preferably get adsorbed on the mild steel surface to inhibit the corrosion in 1 HCl medium. Thermodynamic studies confirmed that the inhibitor molecules chemisorbed onto the metal surface by forming the coordinate bond.

Khanra et al. (2018) have tested the extracts of microalgae in the corrosion inhibition studies of mild steel in acidic medium. It was reported that fatty acidsare the main components of microalgae involved in corrosion inhibition. The authors concluded that the extracts were physisorbed on the metal surface by the electrostatic attractive forces.Leena et al. (2019) evaluated the extract of Lepidagathis keralensis for corrosion inhibition of mild steel in HCl solution. It was reported that the main constituent of Lepidagathis keralensis extract in methanol solution was Phenoxyethene. Thermodynamic calculations concluded that the adsorption of Phenoxyethene molecule through a mixed type of mechanism i.e., both physisorption and chemisorption was occurred on to the mild steel surface.

## 1.7. Scope of Study

### 1.7.1. Importance of acid in industrial process

In the chemical industry acids are the most valuable chemical for the production of various types of drugs, textiles, cosmetics, herbicides, insecticides, polymers and formation of composite materials. In this context, organic acids are among the most versatile ingredients in food and textile industries. Citric, acetic, lactic, tartaric, malic, gluconic, propionic and fumaric acids are some of the organic acids used widely in various industries (Pandey et al., 2008). Without using these compounds, the productions of valuable materials become impossible which are useful for human being. For example, chemical industries use, chloroacetic acid for the manufacturing of carboxymethyl cellulose, carboxymethyl starch derivatives and herbicides such as aryl hydroxyl acetic acid. The same are used for making the insecticide dimethoate and the herbicides benazoline and methyl β-naphthyloxyacetate. A large amount of chloroacetic acid is used for the production of poly vinyl chloride. Chloroacetic acid is also used for manufacturing of drugs such as coumarin and vitamin B6 (Koenig et al., 2008). It is corrosive in nature and damages the equipment (Heitz, 1974).

### 1.7.2. Sustainability and Corrosion Inhibition

During the last couple of decades, research efforts in the field of corrosion and its prevention are extensively studied. This is primarily because of growing interest on good quality, lower cost, depleting the non-renewable natural resources and environmental regulations. These regulations are posing great challenges for anticorrosion research. The corrosion researchers are exploring new strategies to meet the performance, cost and statutory regulations. The ultimate solution is utilisation of our naturally available resources to cut off the prices of raw materials, environmentally benign materials and to add value to a waste material. These maybe formulated as corrosion inhibition of metallic materials. Renewable resources provide cheaper and widely abundant with numerous advantages, such as cost effectiveness, low toxicity, biodegradability and environment friendliness. They yield versatile materials through chemical transformations with plethora of applications, particularly in corrosion resistance against various aggressive medium (Oguzie, 2006; Eddy et al., 2009; Johnsirani, et al., 2013;

Mouryaet al., 2014). Figure 1.3 represents the natural product from various plants as source of corrosion inhibitor.

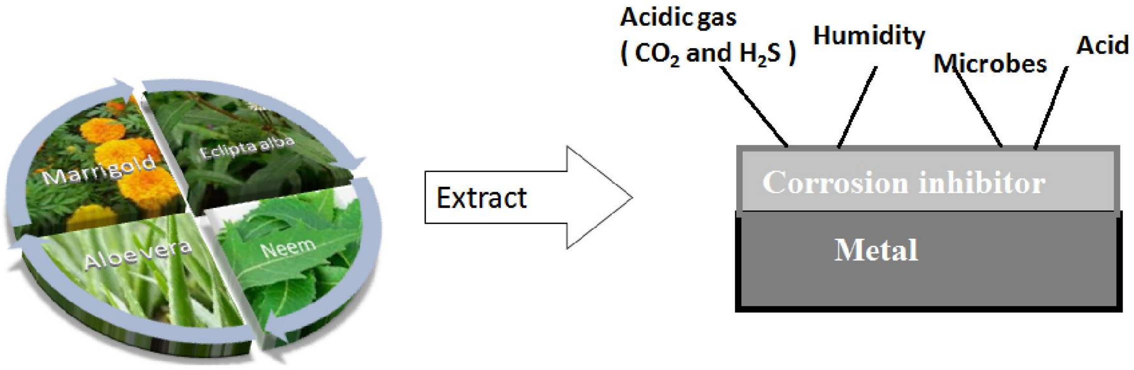


Figure 1.3: Plant based material for corrosion inhibition process for metal in corrosive medium.

## 1.8. Properties of Corrosion Inhibitors

The effectiveness of a corrosion inhibitor depends on following factors:

(i) Strong adsorption onto metal surface

(ii) Increasing or decreasing the anodic and/or cathodic reaction

(iii) Decreasing the diffusion rate for reactants to the surface of the metal

(iv) Decreasing the electrical resistance of the metal surface.

## 1.9. Green Inhibitors

Green corrosion inhibitors are eco-friendly and do not contain heavy metals or other hazardous compounds. An inhibitor is a material (or a mixture of substances) added in a very low concentration to treat the surface of a metal that is uncovered to a corrosive environment that terminates or diminishes the corrosion of a metal.

## 1.10. Outline of Present Work

Carbon steel is the most worldwide used material for industrial and domestic applications because of its good mechanical strength, availability and relatively reasonable cost. However, due to its susceptibility to corrosion attacks, one or more of the corrosion protections is prerequisite prior to its use. Several methods have been investigated and implemented to reduce the corrosion process and extend the life time of the structures including design modification, coating, and cathodic protection. The corrosion inhibition by chemical additives is of great importance and become more common in protecting carbon steel particularly for internal corrosion. However, because of more and more restricted environment regulations, development of a new non-toxic, environment friendly inhibitors are of high priority in corrosion research. As an environmental interest, the use of natural products has received an enhanced attention for greener and safer environmental protection. Several scientific studies have reported different bioactivities of natural products, abundant availability, biocompatibility, low toxicity, and environmental responsibility.

Acid solutions are often used in industry for cleaning, descaling and pickling of steel structures, processes which are normally followed by considerable dissolution of the metal. A useful method to protect metals and alloys in aggressive environments against corrosion is the addition of corrosion inhibitor to the solution in contact with the surface in order to inhibit the corrosion reaction and to reduce the corrosion rate. Large number of organic compounds are studied to investigate their corrosion inhibition potential. Studies revealed that organic compounds especially those with heteroatoms, such as nitrogen, sulphur, oxygen and heterocyclic compounds with polar functional groups and multiple bonds show significant inhibition efficiency

The present study is a step forward in this direction. Plants are even an integral part of human life. Their physical and chemical properties provide not only an invaluable source of food but also a wealth of raw materials, which fulfil daily requirements of fuel, fodder and medicine etc. Considering this, the global interest has increased to utilize the wild plant resources. This scenario has led us to search new alternatives. These species form an important source as a supplement or substitute food at the time of scarcity and play a major role in addressing the nutritional requirement for the inhabitants of the hill region. A wide variety of fruits, roots and other parts of plants are collected from the nature and consumed by rural masses for various applications.

Mizoram is one of the important biodiversity hotspots located in the North East part of India. The intense biodiversity and climate have favoured a complex flora and fauna. Therefore, local tribal have been collected valuable plants for their livelihood and curing diseases. Traditional knowledge is providing them to use medicinal plants for curing antiviral, inflammatory and various other diseases (Hazarika, and Nautiyal, 2012; Kar et al., 2013; Hazarika et al., 2016). The result of literature survey reveals that the plants of this region are still in initial stage of study and phytochemicals are yet to be explored extensively for their chemical and biological behaviour. Therefore, it becomes of great interest to take up the investigation on chemical constituents of certain plants of Mizoram.

In our laboratory, much work is conducted to study the various phytochemicals and we studied the abundantly available folklore medicine such as Eryngium foetidum L, Polygonum plbeium, Mimosa pudica and Prunus cerasoides which are locally used for the treatment of skin disease. We determined the trace element in these selected ethno-medicinal plants, which is part of various enzymes and responsible for curing of skin disease. Trace elements contents in the selected traditional medicinal plants used for curing skin diseases by Mizo people (Rajan et al., 2014). Analysis of trace elements in these plants revealed that iron concentration was observed with the highest concentration in all the medicinal plants studied as compared to other trace elements recorded. Several studies have shown the important role of iron availability and correlating with the bactericidal effect. It is found the medicinal plants from Mizoram are nontoxic and loaded valuable phytochemicals along with significant amount of trace metals for curing for human disease, which has been already established in studies.

Our focus in the present research plan is to evaluate natural products, which are more specifically the extract from medicinal plants. The plant extract has been studied little in context of environmental engineering and environmental chemistry research. The adsorption and corrosion inhibitive properties of medicinal plants in acid solutions are known for centuries. An increase in the resistance to electrochemical degradation has been observed in various plant extracts. The electrically insulating nature of phytochemical, in contrast with metal, is anticipated to favour the plant extract as a corrosion inhibiting and suppressing agent. We have already observed that crude extract from medicinal plant can act as an anti-corrosive agent.

In continuation of our earlier work on medicinal plant, the present work is focussed to investigate the corrosion inhibition properties of some commonly available medicinal plant in Mizoram, India. For the same, five plants are selected on account of their anti-corrosion based primarily on the literature survey along with their several uses in day to day life of people. In the present work, extract of plants is investigated to find a promising corrosion inhibitor for carbon steel. In plants a class of chemical compounds sharing the functional group in which hetero-atom are found. The nontoxic nature of such plants makes the investigation, for its corrosion inhibition property, valuable to produce environmentally friendly inhibitors. Only a few studies have been carried out testing and evaluating plant extract from north east region as corrosion inhibitor for mild steel as illustrated in the literature review chapter. For the present study, we have selected five following plants for evaluation of anti-corrosive property.

### 1.11.1. Allium hookeri

Classification

| | |
|---|---|
| Family | Amaryllidaceae |
| Subfamily | Allioidae |
| Genus | Allium |
| Species | hookeri |

Figure 1.4: Allium hookeri.

Figure 1.4 shows the image of Allium hookeri (Eng. Hookeri chives, Mizo-Mizopurun), which is used in Mizoram as a condiment and vegetable soup and it is a perennial plant with fibrous root system. The plant is having a wide distribution on Mizoram hills. This herb has been used as a flavouring agent and treatment of various diseases. It was found that A. hookeri is not only beneficial biologically, but also it has corrosion inhibiting property to control corrosion reaction of some metallic material.

A. hookeri contains the trace elements, which may play a role in the control of corrosion process by synergetic effect. This is reason to investigate chemical elements and compounds present in A. hookeri fibrous root. The objective of the present study is to carryout phytochemical screening after evaluating its methanolic extract for corrosion inhibiting property.

### 1.11.2.Clerodendrum colebrookianum

Classification:

| | |
|---|---|
| Family | Lamiaceae |
| Genus | Clerodendrum |
| Species | colebrookianum |

Figure 1.5: Clerodendrum colebrookianum walp.

Figure 1.5 shows the image of Clerodendrum colebrookianum walp, it is a shrub and grows on slope of hills in Mizoram. According to some traditional healers, decoction of the leaves is used for the treatment of various diseases. A leafy part of plant is taken as a vegetable. It has been observed that wild edible plant species Clerodendrum colebrookianum have high nutritive value. This is the reason Mizo people traditionally used as vegetable for health. It is popular among local people to control blood pressure.

### 1.11.3. Elsholtzia communis

Classification

| | |
|---|---|
| Family | Lamiaceae |
| Genus | Elsholtzia |
| Species | communis |

Figure 1.6: Elsholtzia communis (a) leaves (b) inflorescence.

Figure 1.6 shows the image of Elsholtzia communis, this plant widely used in medicine, herbal tea, food, spices, and as a vegetable in their diet by Mizo people. These herbs are popular for flavouring agent in various local food items in Mizoram. So, evaluating their Phyto-constituents can help to understand the worth of this plant species.

### 1.11.4. Melocanna baccifera

Classification

| | |
|---|---|
| Family | Poaceae |
| Genus | Melocanna |
| Species | baccifera |

Figure 1.7: Melocanna baccifera.

Figure 1.7 shows the image Melocanna baccifera (bamboo) and it is commonly found in Mizoram and shoot of this plant used as a favoured vegetable by local community. Literature surveys and reports of phytochemical analysis have shown that the bamboo contains several important organic compounds. This study establishes the effectiveness of plant extracts as corrosion inhibitor.

### 1.11.5. Spilanthes acmella

Figure 1.8 shows the image of Spilanthes acmella (para-cress or toothache plant). It is a medicinal plant and Mizo people call it “Ankas”. It has been used as a traditional medicine for toothache, rheumatism and sore throat. This plant is also popular in Mizoram due to pungent taste as vegetable form. The survey demonstrates that this plant is beneficial for human health and is rich in bioactive components, which may play important role in corrosion inhibition of mild steel in acidic medium.

Classification

| | |
|---|---|
| Family | Compositae |
| Genus | Spilanthes |
| Species | acmella |

Figure 1.8: Spilanthes acmella.

# 2. Methodology

Iron and its alloys are widely used as parts of military ammunitions, electronics, home appliances, industry and medical equipment. However, the mild steel is vulnerable towards the corrosion attack (Waseda and Suzuki, 2006). Surface modification is therefore required to minimize its corrosion and extend the life of same in corrosive environments. There are a variety of physical and chemical treatments like coating, anodizing and inhibitors, which are used for the metal–solution interface and act as a barrier by separating the metal surface from the corrodent (de la Fuente et al., 2011). The use of inhibitors is one of the most practical methods for protection of metal in aggressive medium.

The present chapter deals with the description of methods used in characterization of the plant material and the corrosion monitoring techniques. The corrosion inhibitive effect of root of Allium hookeri, leaves of Clerodendrum colebrookianum, inflorescence of Elsholtzia communis, leaves of Melocanna baccifera and aerial part of Spilanthes acmella in 1N HCl on mild steel was carried out using weight loss, potentiodynamic polarization, and electrochemical impedance methods. Moreover, the surface morphology and characterization of samples were conducted by the FT-IR and SEM.

## 2.1. Material

### 2.1.1. Inhibitor

In the modern time, traditional and herbal medicines including edible plants are in practice to use as raw material in industries for the production of valuable organic compounds because of its natural abundance and cost effectiveness. Many medicinal plants are often used at commercial level. Economically important plants serve as sources of valuable industrial products. Nowadays, new trend has emerged to use the prevention of metal corrosion during its finishing process. It has been a great success in the industry due to its eco-friendly nature and for contaminant free environment. Hence, we are interested to characterize the phytochemicals as possible corrosion inhibitors.

The medicinal plant products are selected for the present research work. Selection of medicinal plant is important in development of a plant based herbal medicine and non-poisonous eatable products. Present study is focused on analyzing the corrosion inhibition properties of selected plants in 1N HCl. These plants have been used for the treatment of various diseases and the medicinal values of these extracts are due to presence of active phytoconstituents present (Khomdram et al., 2011; Yomgam et al., 2017).

On the basis of leads available from folk usage and experimental studies Allium hookeri, Clerodendrum colebrookianum, Elsholtzia communis, Melocanna baccifera and Spilanthes acmella are selected, which are widely distributed in Mizoram, India. The alcoholic fractions of these plants are reported for antidiabetic, anti-hypercholesteremia and anthelmintic activity (Nath and Bordoloi, 1991; Bhardwaj and Gakhar, 2005). However, the corrosion inhibition activities of these plant extracts are yet to be explored.

The selective plants are purchased from local markets of Aizawl, washed thoroughly with distilled water and dried at room temperature for 10 days. Infected part of plant samples is discarded due to loss of important phytochemical. Plant samples are washed under running distilled water and shade drying for higher composition of chemical constituents. Drying the plants is the most important part as it helps in retaining the active ingredients in its natural form in the dried herbal preparation. Further, it is important to extract the active phytochemical constituents and recommended method in retention of plant compounds.

### 2.1.2. Solvent

The most suitable solvent for the extraction of phytochemicals is aqueous methanol. The methanol is known as a good solvent for phytochemical extraction as it is safe for human consumption and easy to distillate off (Thouri et al., 2017). From the point of easy handling, evaporation and further solubility in acidic medium methanol is appropriate solvent used for extraction of phytochemical.

The shade dried plant was grinded to make fine powder using a mechanical grinder (Bajaj Mixer grinder). Fifty-gram of dried powder was soaked in 500 mL of solvent keeping the solvent to sample ratio 10:1 (v/w). 60% methanol was used as solvent and the extraction was conducted for 24 h at room temperature. The extract was filtered using Whatman No.1 filter paper. The filtrate was collected and the residue was re-extracted to enhance the extractants (Dhanani et al., 2017). Fresh solvents were added to the residue at the same ratio and again kept for 24 hours. This step was repeated three times in order to achieve maximal extraction of active compounds. Dried crude extracts were weighed and kept at 5°C till its further use.

### 2.1.3. Gas Chromatography- Mass Spectrometry

Separation of plant phyto-constituents were separated and identified using the chromatographic technique. The chromatography works on the basis of differential affinities to the stationary phase and mobile phase (Coskun, 2016). The choice of technique depends upon the solubility and volatilities. Gas chromatography (GC) is the best method for separating the components. The GC and Mass spectroscopic (MS) techniques are important analytical tools for the separation and determination of natural products (Patelet al., 2010; Yuan Bi-Feng, 2014). Qualitative and quantitative analysis of phytochemicals could be done using the gas chromatography/mass spectroscopy (GC-MS).

The GC-MS analysis of the crude methanolic extracts of the plants was performed using the Autosystem XL Gas Chromatograph (Perkin-Elmer instrument, USA) equipped with Turbo Mass Spectrophotometer (Perkin-Elmer instrument, USA) at Sophisticated Instrumentation Centre for Applied Research and Training (SICART) Vallabh Vidyanagar Gujarat, India. The GC-MS method was operated by using electron impact ionization technique with two fused silica capillary columns, 30 × 0.25 mm ID, coated with D-I, 0.25 µm film. Helium was used as a carrier gas at constant pressure of 100 kPa, injection port temperature of 523 K and flow rate was maintained to 20 mL/min. Temperature programmed: 343 K- 523 K at the increasing rate of 10 °C/min was used at 70 °C for 5 min and it was raised by 10 °C/min up to 250 °C after which it was kept on hold for 15 min. Chromatographic data were processed with the mass detector operated with electron impact ionization (EI) mode with ionization energy 70 eV. Samples dissolved in methanol were run fully in the range of 60-750 amu and the injection volume was 1µL. The obtained mass spectra of plant extract were measured by an AMDIS (Automated Mass Spectral De-convolution and Identification System) and transferred to the National Institute of Standards and Technology (NIST) Mass Spectral library Search Program.

## 2.2. Methods

Corrosion inhibition is divided into four general categories: cleaning, inhibitor preparation, measurement of corrosion rate and confirmation of adsorption. The metallic surface after visual inspection was followed by weight measurement and finally image of metal in presence and absence of inhibitor was taken under SEM imaging. The determination of corrosion rates was determined on the basis of weight loss during the exposure in corrosive medium (Fontana and Greene, 1986; Heitz et al., 1992; Shreir et al., 1994; Koch et al., 2016).

### 2.2.1. Material Preparation

Shape and morphology of the metal play an important role in obtaining uniform corrosion rate in the corrosive medium. Microscopic investigation of corrosion product requires extra care in the preparation of metal specimens. The most important for corrosion inhibition, the structure of the metal surface must be taken flat, scratch-free and mirror surface. Mild steel (MS) was cut into rectangular shape of 2 x 2 x 0.5 cm size containing 0.09 wt. % (C), 0.51 wt. % (Mn), 1.5 wt. % (Cr), 0.0219 wt. % (Si), 0.012 wt. % (P); 0.009 wt. % (Ni), remaining iron. The sheet was used for present study. Mechanical and chemical cleaning techniques were used to remove organic and inorganic contaminants present on the surface of metallic sheet. They were invariably used to remove corrosion products from the metal surface. Before each test, specimens were successively polished (mechanical cleaning) with different grades of emery paper up to 2000 grade and finally, polished with alumina abrasive to obtain mirror finish and washed with acetone to remove organic contaminants from metal surface if any. The same procedures were adopted with mild steel coupons in all measurements. The tests were carried out at various temperatures controlled by a water bath.

### 2.2.2. Measurement of Corrosion Rates

There are three main methods that are used to measure the corrosion rate (Bardel, 2004):

a) Reduction in thickness of the metal per unit time: Measurement of corrosion rates for mild steel by thickness reduction per unit time is most significant method. In the metric system this may be expressed as millimeter per year (mm/year) or mils per year (mpy) or inches per year.

b) Weight loss of metal per unit area time: Weight loss per unit area and per unit time is simplest and established method, because weight loss is directly related to surface area of the specimen. In this technique without sophisticated equipment, the result is reliable due to it is direct measurement is obtained without disruption of the metal substrate.

c) Corrosion current density: On this basis of weight losses per unit area/density, it is possible to obtain the corrosion rate which is equivalent to ions losses from metallic specimen. This type of ions losses is expressed as the corrosion current density. It is a directly related with electrochemical reaction as well as measurement for cathodic and anodic protection efficiency of inhibitor molecule in acidic medium.

### 2.2.3. Gravimetric Measurements

Corrosion rate and inhibition efficiency of five plant extracts were estimated by weight loss method. Gravimetric measurements were conducted by suspending the mechanically polished pre-weighed mild steel surface of the mild steel sample in 100 mL test solutions for specific time period (3h) with and without addition of different concentrations of plants extracts (0.1g/L-0.5 g/L) at temperature range 300 K – 333 K. Then the corroding specimens were washed with water followed by acetone and dried for its weight measurement.

The variation of corrosion rate ($C_{rate}$) and inhibition efficiency (%IE) as a function of inhibitor concentration in acid media in absence and presence of methanolic extract of plants were calculated by standard method given in literatures. $C_{rate}$ and %IE were calculated by using following equations:

$$\frac{\quad}{\quad \times \quad} = \frac{\Delta}{\quad} \qquad (1)$$

$$\% \quad = \frac{(\quad) \quad (\quad)}{(\quad)} \; 100 \qquad (2)$$

Where, W is the average weight loss in mg, A is the total area of MS specimen 6.6572 $cm^2$ for all studies, t is the immersion time (3h). In equation 2, $C_{rate\ (blank)}$ and $C_{rate(inh)}$ are the corrosion rates without and with inhibitor, respectively. The covered surface area of the mild steel specimens after exposing to 1 N HCl solution in absence and present of the inhibitors is given as:

$$= \frac{(\% \quad)}{\quad} \qquad (3)$$

### 2.2.3.1. Adsorption Isotherm

The inhibition mechanism of inhibitors was estimated by θ values, which has been determined from gravimetric analysis at different concentrations of plant extracts. Langmuir’s adsorption isotherm is the simplest one and tested at first. A correlation between θ and inhibitor concentration in acidic medium for Langmuir’s adsorption model is reported by various workers as (El-Haddad, 2016)

$$\frac{\quad}{\quad} = \frac{\quad}{\quad} + \qquad (4)$$

where $K_{ads}$ is the equilibrium constant for adsorption-desorption equilibrium ($K_{ads}$) and $C_{inh}$ is the inhibitor concentration in g/L. $C_{inh}/\theta$ versus $C_{inh}$ was plotted at a constant temperature (300 K-330 K).The equilibrium constant related to standard free energy of adsorption (ΔG ) as follows:

$$= \frac{}{.} \quad \left(\frac{\Delta}{}\right)$$

(5)

where R is gas constant, T is the working temperature and 55.5 is the value of concentration of water in solution in mol/L.

### 2.2.3.2. Temperature Effect

A rise in the temperature of the corrosive medium accelerates the hydrogen evolution process and hence the corrosion rate. The decrease in %IE and increase in the corrosion rate with rise in temperature is attributed to desorption of the inhibitor molecules from the mild steel surface and increase in exposure area of metal surface in corrosive acidic medium. The decrease in the adsorption at higher temperature indicated that physical adsorption of inhibitor took place onto the mild steel surface.

The adsorption of inhibitors on the metal surface depends on the structure and electronic properties of inhibitor molecules, electrochemical potentials at the metal-test solution interface and the temperature of corrosive medium. The effect of temperature on the corrosion rate and inhibition efficiency of plant extracts for mild steel corrosion in 1 N HCl was studied using weight loss methods. Further, the inhibition efficiency, adsorption constant, correlation coefficient and ΔG obtained by weight loss measurements in presence of extract at different concentrations (0.1g/L – 0.5g/L) and temperatures (300 K- 333 K) are presented. The values of apparent activation energy

($E_a$) for corrosion process were calculated in absence and presence of different concentrations of inhibitors using Arrhenius equation:

$$-\frac{\qquad}{\cdot} \quad + \tag{6}$$

Where, $E_a$ is the apparent activation energy, A is the frequency factor, T is the absolute temperature and R (8.314 J/ mol K) is the molar gas constant. The change of enthalpy of activation ($\Delta H_a$) and change of entropy of activation ($\Delta S_a$) for corrosion reactions were determined through Eyring transition state equation:

$$= \frac{\quad}{}\exp \frac{\Delta}{\quad} \exp \frac{\Delta}{\qquad} \tag{7}$$

here and are Plank's constant and Avogadro number, respectively. The rest of the terms have their usual meaning. Plots of logC /T versus 1/Tfor blank and for different concentrations of plant extracts gave straight lines with a slope ($-\Delta H_a/2.303R$) and an intercept of [(log(R/Nh) + ($\Delta S_a/2.303R$)] on y-axis of these straight lines. The values of E and $\Delta H_a$ are close to each other as expected for the corrosion process in electrolytic solution.

### 2.2.4. Electrochemical Measurements

The electrochemical measurements were performed using AUTOLAB (PGSTATE 12/20/302; Netherland) Potentiostat instrument with GPES software assembled with three electrodes at 300 K. A mild steel specimen in test electrolytic solution with an exposed area of 0.75 $cm^2$ was used as working electrode. Graphite rod and Ag/AgCl electrode with Luggin capillary were used as counter and reference electrodes, respectively. The exposed surface area of counter electrode is also 0.75 $cm^2$. Prior to each measurement for polarization curves and electrochemical impedance spectroscopy (EIS), the MS specimens were mechanically abraded with emery papers from 80 grit to 2000 grit, respectively and then exposed to the corrosive medium at steady-state open circuit potentials (OCP) for 3h at 300 K to attain an equilibrium state. The polarization resistance was measured for MS specimen in 1 N HCl in absence and presence of different concentrations of plant extract in the potential range from -0.650 V to 0.650 V versus OCP at a scan rate of 0.001 V/s.

Electrochemical impedance spectroscopic (EIS) studies were carried out in inhibiting and non-inhibiting electrolytic solutions with similar three electrodes configuration as per the polarization study using a Gamry Instruments Reference 600 Potentiostat/Galvanostat/Zero Resistance Ammeter (ZRA). Impedance measurements were performed at open circuit potential (OCP) by the application of a periodic small amplitude (10 mV) ac voltage signal with a wide spectrum of frequency range from 100 kHz to 0.01 Hz. The impedance data was analyzed using the Nyquist plots. All the above measurements were repeated thrice for reproducibility of results and an average value was reported.

#### 2.2.4.1. Potentiodynamic Polarization Measurements

The cathodic and anodic current – potential were measured for MS specimens in absence and presence of various concentrations of plants extract (0.1 – 0.5 g/ L) in 1 N HCl solutions at 300 K using Tafel polarization method. The electrochemical parameters such as corrosion current density ($I_{corr}$), corrosion potential ($E_{corr}$) and cathodic and anodic Tafel slopes ($\beta_a$ and $\beta_c$) were extracted by extrapolation of the linear segments of the cathodic and anodic curves up to their interaction.

The $C_{rate}$ and θ of MS specimen in 1 N HCl solutions with and without different concentrations of plant extract were calculated by Tafel polarization data using following equations:

$$( \qquad ) = \frac{.}{\qquad\qquad} \tag{8}$$

$$\theta = \frac{( \qquad ) \qquad ( \quad )}{( \qquad )} \tag{9}$$

$$(\%) = \quad 100 \tag{10}$$

Where $C_{rate}$ is corrosion rate in mm/year, $I_{corr}$ is corrosion current density in A/cm$^2$, EW is equivalent weight of mild steel specimen in gram/equivalent and D is density of the specimen under investigation.

### 2.2.4.2. Electrochemical Impedance Spectroscopy (EIS)

EIS has been performed to confirm the adsorption of inhibitor molecules on to the MS surface. This study provides the information regarding metal dissolution in corrosive medium through electrochemical characteristics such as metal/solution interfacial double layer capacitance ($C_{dl}$), charge transfer resistance ($R_{ct}$) and solution resistance ($R_s$), which are extracted from intercept at the high frequency region and at the low frequency region ($R_{ct}$) on the real and imaginary axes, respectively. The impedance spectra were analyzed by fitting to the equivalent circuit model, which built by the Z-view software. The $C_{dl}$ was calculated by following equation:

$$= \frac{}{\qquad\qquad} \tag{11}$$

where $f_{max}$is the frequency at which imaginary part of the impedance is maximum. The Nyquist plots (impedance diagram) obtained by measuring the AC impedance for mild steel in 1 N HCl solution in the absence and presence of various concentrations of plants extracts.

### 2.2.5. Fourier Transform Infrared (FT-IR) Spectroscopic and Scanning Electron Microscopic (SEM) Analyses

FT-IR analysis was carried out to identify the bonding sites present in the methanolic extract of plants as well in the abraded protective films of mild steel surface as dissolved in the highest concentration of plant extract in 1 N HCl solution for 3 h at 300 K and 303 K (Gadow et al., 2017). The test solutions were applied on the glass plate and the FT-IR data recorded in the wave number range 4000-400 $cm^{-1}$ using the Perkin-Elmer 2000 FT-IR spectrometer.

The microscopic studies for the effect of plant extract onto corrosion reaction, metal dissolution and structural change of mild steel were carried out using the Scanning Electron Microscopic (SEM) imaging technique. It was used to identify the grain size and its distribution as well the intensity of corrosion product on metal surface by which corrosion inhibitive properties of the inhibitor on metal surface was confirmed. The result of microstructure studies indicated the corrosion of metal and expected behavior in a given corrosive medium.

The surface morphology of the mild steel samples in pure state as well as after immersion in 1 N HCl with and without highest concentration of plant extracts were investigated using methanolic extract of plant extracts exposed for 3 h at 300 K using A Carl Zeiss LEO SUPRA 50VP FE-SEM at an accelerating voltage at 15 keV. The mild steel specimens were carefully polished as described above and then the specimens were cleaned with distilled water, dried prior to its surface analysis.

# 3. Results and discussion

This chapter includes the experimental results and discussion of the present study on corrosion inhibitive action of the five different plant extracts on MS in 1 N HCl solution. The individual behaviour of each plant extract as corrosion inhibitor was briefly analysed and evaluated comparatively.

## 3.1. Selection of Corrosive Chemicals

Cleaning of MS related machinery is necessary for contaminate free production of product in food processing, chemical and pharmaceutical samples. The equipment gives best performance with clean and corrosion free environment. However, cleaning agent themselves corrode the equipment and increase the operational and maintenance costs (Romero et al., 2010). The practice of cleaning the metal equipment before and after installation and its operation is the most important step to maximize the production of good quality products (Rahse, 2014). This includes methods of removing oxide scale, free iron contamination, dirt and surface stain, which occur during normal interaction with the surrounding environment.

## 3.2. Extract of Allium hookeri (AH)

### 3.2.1. Phytochemical analysis of AH Extract by GC-MS

The inhibitive action of extracts of aromatic herbs, spices, and medicinal plants on metals and alloys corrosion in different acidic media at their optimum concentrations and temperature were reported previously (Raja and Sethuraman, 2008). The recent work on natural product extracts as green corrosion inhibitors has shown remarkable limitations due to lack of appropriate phytochemical investigation. This is worth to mention here that the present study includes the detailed phytochemical investigation of the crude methanolic extract of AH roots using GC-MS, which helps to identify the major corrosion inhibitive components present in it. The analysis of GC-MS data of AH extract with the help of National Institute Standard and Technology (NIST) having more than 62,000 patterns (Ezhilan and Neelamegam, 2012) helps to identify several organic ingredients having different structures. The GC-MS spectra and corresponding NIST library database revealed the presence of major components as glucose derivatives viz., 2-penten-1-ol, isosorbide and mannitol. These identified compounds are listed in Table 3.2.1. Figure 3.2.1 shows the presence of glucose derivatives such as 2-penten-1-ol and isosorbide with O-atom and π-bonds in AH extract. Inhibitive action of the extract of carbohydrate derivative is already reported by Yadav et al (2016). They found carbohydrate derivatives as a probable inhibitive molecule in natural plant extract.

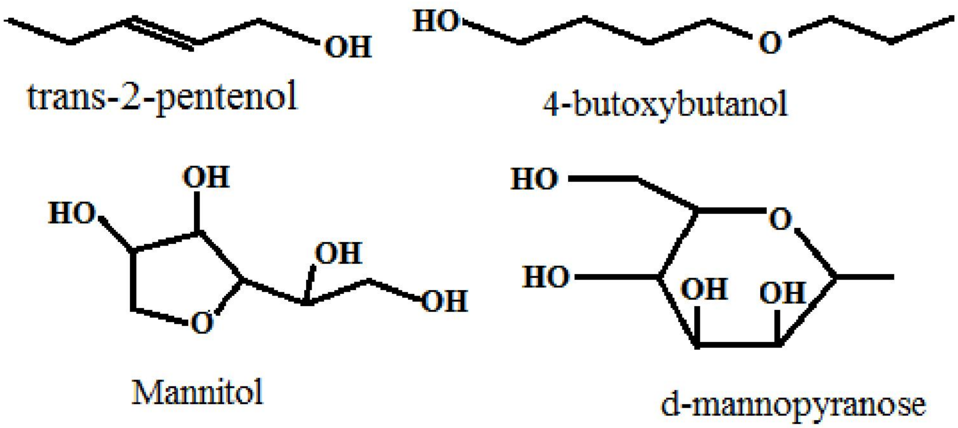


Figure 3.2.1: Main phytochemical constituents in AH extract.

Table 3.2.1: Chemical constituents present in the AH extract using the GC-MS analysis.

| Hit | Rev | For | Compound name | M.W. | Formula | CAS |
|---|---|---|---|---|---|---|
| 1 | 854 | 710 | Alpha. -d-mannopyranoside, methyl 3,6-anhydro | 176 | $C_7H_{12}O_5$ | 15814-56-9 |
| 2 | 828 | 699 | 1-butanol, 4-butoxy | 146 | $C_8H_{18}O_2$ | 4161-24-4 |
| 3 | 825 | 718 | 1,3-propanediol,2-ethyl-2-hydroxymethyl | 134 | $C_6H_{14}O_3$ | 77-99-6 |
| 4 | 825 | 722 | Sucrose | 342 | $C_{12}H_{22}O$ | 11 57-50-1 |
| 5 | 816 | 745 | 2-deoxy-d-galactose | 164 | $C_6H_{12}O_5$ | 1949-89-9 |
| 6 | 809 | 684 | 1,3-propanediol,2-ethyl-2-hydroxymethyl | 134 | $C_6H_{14}O_3$ | 77-99-6 |
| 7 | 804 | 710 | Beta. -d-glucopyranoside, methyl 3,6-anhydro- | 176 | $C_7H_{12}O_5$ | 3056-46-0 |
| 8 | 796 | 565 | 1,2-epoxy-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy) propane | 420 | $C_{11}H_9O2F_{13}$ | 122193-68-4 |
| 9 | 791 | 655 | 2-penten-1-ol, (e) | 86 | $C_5H_{10}O$ | 1576-96-1 |
| 10 | 781 | 693 | (2s,3s) -(-)-3-propyloxiranemethanol | 116 | $C_6H_{12}O_2$ | 89321-71-1 |
| 11 | 770 | 631 | Beta. -d-glucopyranose, 4-o-. beta. -d-galactopyranosyl | 342 | $C_{12}H_{22}O_{11}$ | 5965-66-2 |
| 12 | 769 | 707 | Isosorbide dinitrate | 236 | $C_6H_8O_8N_2$ | 87-33-2 |
| 13 | 768 | 685 | d-mannitol, 1,4-anhydro- | 164 | $C_6H_{12}O_5$ | 7726-97-8 |
| 14 | 762 | 564 | Hydroperoxide hexyl | 118 | $C_6H_{14}O_2$ | 4312-76-9 |
| 15 | 756 | 684 | Isosorbide | 146 | $C_6H_{10}O_4$ | 652-67-5 |
| 16 | 755 | 487 | d-mannitol, 1,4-anhydro- | 164 | $C_6H_{12}O_5$ | 7726-97-8 |
| 17 | 755 | 661 | d-erythro-pentose, 2-deoxy- | 134 | $C_5H_{10}O_4$ | 533-67-5 |
| 18 | 752 | 638 | 2,4,4-trimethyl-1-pentanol | 130 | $C_8H_{18}O$ | 16325-63-6 |
| 19 | 750 | 473 | 1,3;2,5-dimethylene-l-rhamnitol | 190 | $C_8H_{14}O_5$ | 900128-41-1 |
| 20 | 746 | 664 | Alpha. -d-glucopyranoside, methyl 3,6-anhydro- | 176 | $C_7H_{12}O_5$ | 13407-60-8 |

### 3.2.2. Gravimetric measurements of AH Extract

#### 3.2.2.1. Effect of AH Concentration

Table 3.2.2 illustrates a rapid decrease in corrosion rate with increasing concentration of inhibitor. This is due to the fact that more inhibitor molecules are adsorbed onto the MS surface and hence, adsorption coverage eventually increases the concentration of inhibitor, which protects effectively the MS surfaces from aggressive medium (El-Etre and Abdallah, 2000). It is also observed from Table 3.2 that surface coverage (θ) increases with the increase in inhibitor concentrations at working temperature 300 K. Similar trends were observed by Umoren et al (2004) and found efficient inhibition activity in aqueous and methanolic extract of coconut.

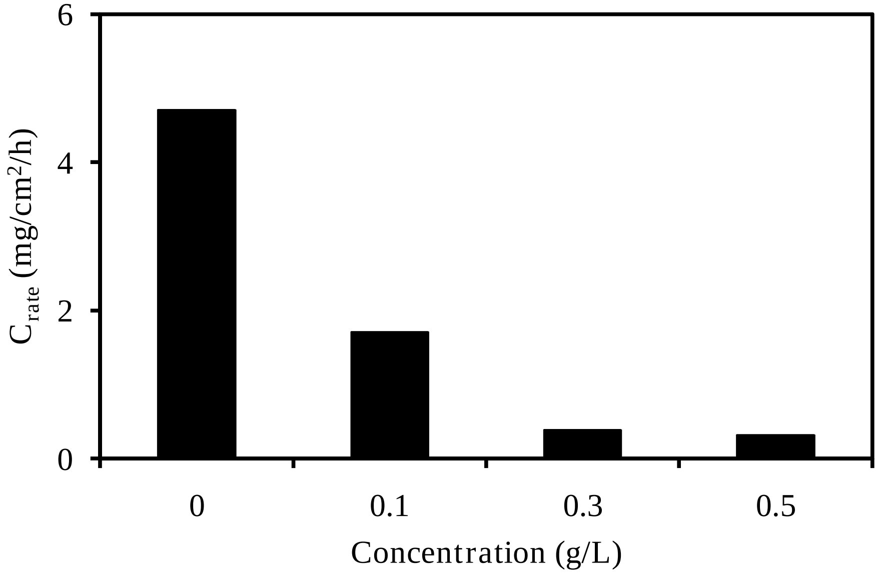


Figure 3.2.2: Variation of corrosion rate with presence of different concentration of AH extract in 1 N HCl at 300 K.

The corrosion rate of MS in 1 N HCl was observed as 4.71 mg/cm$^2$/h which is decreased to 0.32 mg/cm$^2$/h in present of 0.5 g/L AH extract with 93% surface coverage over MS surface.This is due to the formation of protective film of inhibitor molecule on the MS surface (Avci and Keleş, 2011).The corrosion inhibition efficiency at different concentrations of methanolic extract of AH in 1 N HCl solution has been obtained through weight loss measurements at temperature 300 K. Table 3.2.2 reveals that the inhibition efficiency increases linearly with increasing the inhibitor concentrations.

Table 3.2.2: Weight loss results for MS in 1N HCl in the absence and presence of various concentration of AH extract.

| Conc. (g/L) | $C_{rate}$(mg/cm$^2$/h) | %IE | θ |
|---|---|---|---|
| Blank | 4.71 | --- | --- |
| 0.1 | 1.71 | 63 | 0.63 |
| 0.3 | 0.39 | 91 | 0.91 |
| 0.5 | 0.32 | 93 | 0.93 |

### 3.2.2.2. Effect of Temperature

Figure 3.2.3 shows the inhibition efficiency as a function of temperatures. It is evident from the figure that increasing the temperature causes to decrease the corrosion reaction. This indicates that the AH is adsorbed on the MS surface physically. Similar results were reported for Punica granatum peel extract in corrosion behaviour (Behpour et al., 2012) In recent times, among the various natural products, such as the extract of Retama retam extracts (Benmenine et al., 2014)), Mangifera indica and Citrus sinensis fruit peel extracts (Cardozo da Rocha et al., 2010), Chlorophytum borivilianum root extract (Ji et al., 2013), Anacyclus pyrethrum extracts (Benali et al., 2014), Chlorophytum borivilianum root extract (Ji, et al., 2013) are found to be effective corrosion inhibitors for steel in various corrosive solutions. The inhibition effect of the Seaweed extract on the corrosion of MS in saline solution was reported by Deyab (2016). Maximum inhibition efficiency of 93% was reported with 1.2 % (v/v) Seaweed extract at 298 K in saline solution. They also reported that the polysaccharide as carbohydrate is a major constituent of seaweed that inhibits corrosion effectively in saline solution.

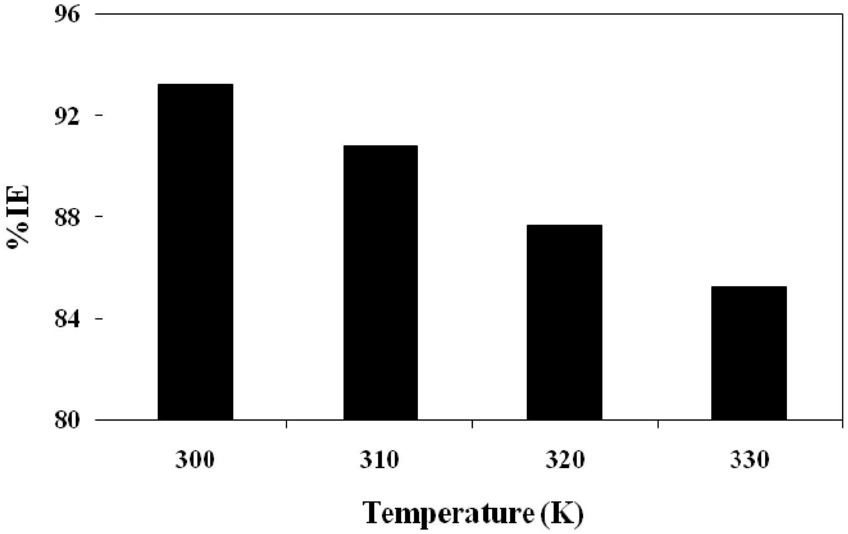


Figure 3.2.3: Variation of corrosion inhibition efficiency with temperature for 0.5 g/L of AH in 1 N HCl.

### 3.2.2.3. Adsorption Isotherm

The Langmuir adsorption isotherm plots presented in Figure 3.2.4, show straight lines and from the value of surface coverage, $K_{ads}$ was calculated and reported in Table 3.2.3. It is well established that value of $K_{ads}$ represents the strength of adsorption of inhibitor molecules in presence of various concentrations of AH extracts on the metal surface. The lower value of $K_{ads}$ with increasing temperature indicates strength of adsorption decreases with temperature and hence; lowers the inhibition efficiency.

Table 3.2.3: Free energy and adsorption parameters of MS in 1 N HCl containing different concentration of AH extracts.

| Temp.(K) | $K_{ads}$ | - (kJ/mol) |
|---|---|---|
| 300 | 17.98 | 17.45 |
| 310 | 14.62 | 17.31 |
| 320 | 12.55 | 16.56 |
| 330 | 10.43 | 16.09 |

It is clear from the Table 3.2.3 that AH shows highest $K_{ads}$ value at lower temperature, which indicates that it possesses strongest adsorption on MS surface. The standard free energy in presence of AH extract at different concentrations (0.1 g/L-0.5 g/L) and temperatures (300 K- 330 K) are then obtained and presented in Table 3.2.3. These results demonstrate that negative value of standard free energy around (–20 kJ/mol), usually pointed towards the physical adsorption. However, such adsorption is not to be concluded as pure physical or chemical adsorption on the basis of free energy value. The lower value of standard free energy, in this study, pointed for dominant physisorption of AH extract on MS surface at all studied temperatures and concentrations.

Arrhenius-type thermodynamic parameters for corrosion process plays an important role in understanding the inhibitive mechanism i.e., in defining the spontaneity of the conversion of metal to corrosion products which is formed in the environment to which the metal was exposed. The rising in activation energy value, compared to the blank solution, was generally interpreted as an indication of the formation of adsorptive film. This fact was governed by a physical (electrostatic) mechanism or a weak chemical bonding between the inhibitor molecules and the metal surface.

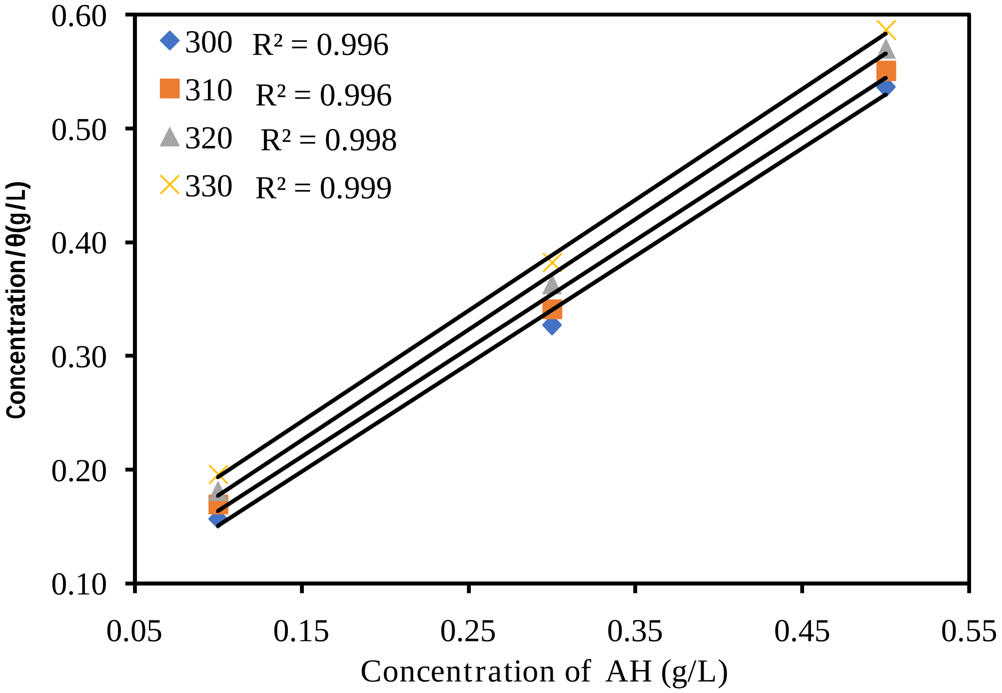


Figure 3.2.4: Langmuir adsorption isotherm for AH extract in 1 N HCl.

From Table 3.2.4, it is clear that activation energy ($E_a$) values in 1N HCl are increased with increasing the inhibitor concentration. The higher values of activation energy tend to create a physical barrier to charge and mass transfer of metal surface. This behaviour resulted the decrease in corrosion rate of MS in presence of inhibitor in acidic medium. The increase in activation energy is considered in terms of Arrhenius equation model as well. The thermodynamic transition state plot of log ($C_{rate}$/T) vs. 1/T for MS at various concentrations of AH, resulted with straight lines, as shown in Figure 3.2.6. Inspection of Table 3.2.4, reveals that the $\Delta H_a$ values for dissolution reaction of steel in AH extract containing solution i.e., in presence of inhibitors are higher (42.28 kJ/mol - 59.29 kJ/mol) than that of the absence of inhibitors (34.04 kJ/mol). The positive signs of $\Delta H_a$ reflect the exothermic nature of steel dissolution process suggesting that the dissolution of steel is slower in presence of inhibitor. Higher value of $\Delta H_a$ in presence of inhibitor indicates that energy barrier is raised for corroding reaction in presence of inhibitor in aggressive solution. The entropy of activation ($\Delta S_a$) in absence of inhibitor is higher due to the extent of more metal dissolution and presence of the inhibitor.

Table 3.2.4: Thermodynamic parameters for MS dissolution in 1 N HCl solution in the absence and presence of various concentration of AH extract.

| Conc.(g/L) | Δ (kJ/mol) | -Δ (J/mol/K) | $E_a$ (kJ/mol) |
|---|---|---|---|
| Blank | 34.04 | 118.64 | 36.62 |
| 0.1 | 42.28 | 99.09 | 44.85 |
| 0.3 | 57.88 | 59.63 | 60.63 |
| 0.5 | 59.29 | 57.36 | 61.84 |

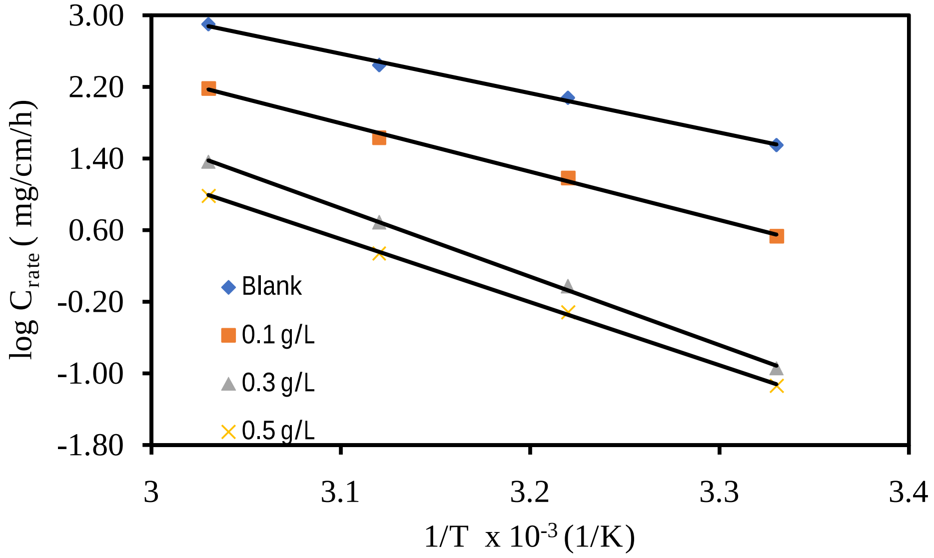


Figure 3.2.5: Arrhenius plot for MS in 1 N HCl with and without AH extract.

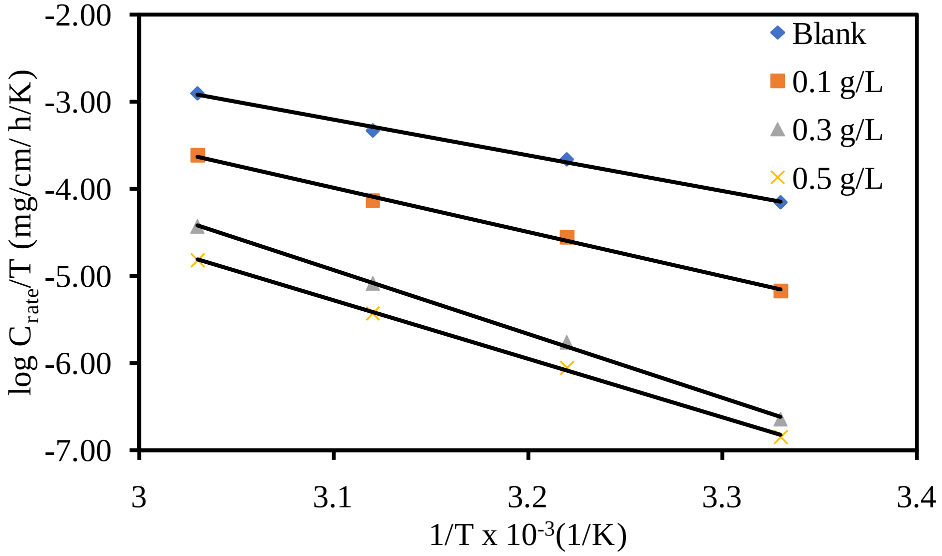


Figure 3.2.6: Transition state plot for MS in 1 N HCl containing different concentration of AH extracts.

### 3.2.3. Electrochemical Measurements of AH Extract

### 3.2.3.1. Measurement of Potentiodynamic Polarization of AH Extract

Figure 3.2.7, shows the potentiodynamic polarization behaviour of MS in 1 N HCl solution with and without different concentrations of AH (0.1 - 0.5 g/L) at temperature 300K. The MS was exposed to test solutions for three hours with suitable arrangement of electrode for the study.

Electrochemical parameter such as corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$), cathodic and anodic Tafel slopes ($ß_c$ and $ß_a$) which governs the corrosion rate and inhibition efficiency. The cathodic and anodic polarisation of MS in absence and presence of AH extract having different concentrations in well-defined Tafel plots are obtained (Aribo et al., 2016) and illustrated in Figure 3.2.7. It is observed from the Figure 3.2.7, that $I_{corr}$ decreases with increasing concentration of AH extract in acidic media. The change of cathodic and anodic Tafel slopes in blank and in presence of varied concentrations of the inhibitor was also compared. This result indicates that the AH extract suppressed both the anodic and cathodic reactions (Bommersbach et al., 2005).

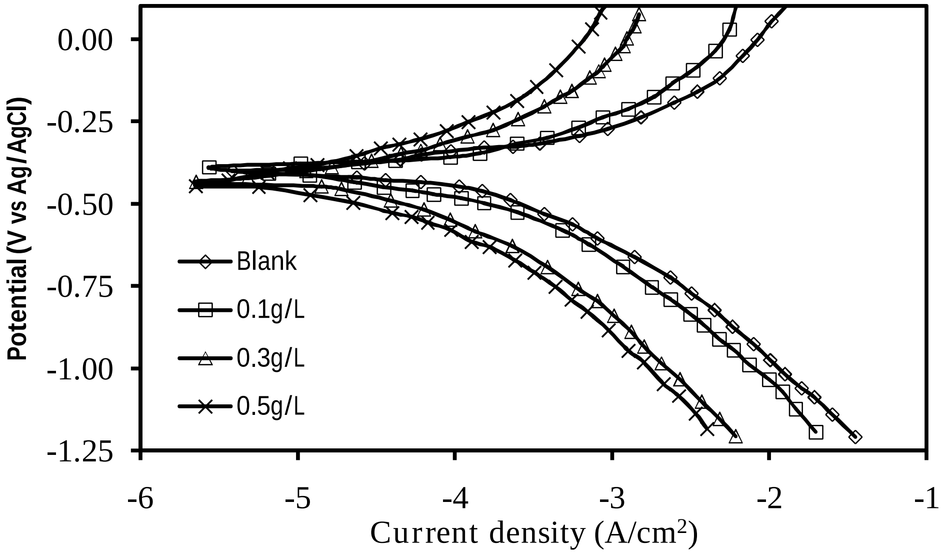


Figure 3.2.7: Tafel polarization curves for MS in 1N HCl in absence and presence of various concentrations AH extract.

Inspection of Figure 3.2.7 and Table 3.2.5 reveals that the corrosion potential shifted towards more negative value and cathodic curves shifted towards lower current densities in presence of plant extract as compared to blank. This is due to adsorption of inhibitor extract over the cathodic active corroding surface and decrease in corrosion rate. It is also observed that the anodic branches shifted towards lower corrosion current density with increasing the concentration of inhibitor and higher value of $ß_a$ over $ß_c$. It means that the cathodic inhibition reaction is predominant.

Table 3.2.5: Tafel polarization parameters for MS corrosion in 1N HCl in the presence and absence of AH extract.

| Conc. (g/L) | $\beta_a$ (mV/dec) | $-\beta_c$ (mV/dec) | $I_{corr}$ (µA/cm$^2$) | $-E_{corr}$ (mV vs Ag/AgCl) | %IE |
|---|---|---|---|---|---|
| Blank | 275 | 415 | 397 | 385 | -- |
| 0.1 | 142 | 361 | 138 | 355 | 65 |
| 0.3 | 253 | 403 | 68 | 377 | 82 |
| 0.5 | 231 | 377 | 52 | 483 | 86 |

These observed results indicate that inhibitor suppresses the dissolution of iron whereas the variation of cathodic Tafel slope suggests the suppression of the hydrogen evolution reaction in presence of AH extract. Table 3.2.5 shows that corrosion current density is significantly decreased i.e., from 397 µA/cm$^2$ to 52 µA/cm$^2$ and the corrosion inhibition efficiency is increased from 65.30 % to 86.60 % with an increase in inhibitor concentration form 0.1 g/L to 0.5 g/L. The similar results were also reported with other corrosion inhibitors. It was observed from the data that the addition of A. hookeri plant extract decreased the corrosion current density ($I_{corr}$). The decrease was due to the adsorption of the inhibitor on metal surface in acid solution. The efficiency of corrosion was obtained maximum at the concentration of 0.5 g/L. This result was in good agreement with the weight loss measurement (Gadow et al., 2017)

### 3.2.3.2. EIS of AH extract

EIS is one of the most important and easiest electrochemical tools to study the corrosion inhibition reaction. It helps to monitor the interaction between electrode and electrolyte in absence and presence of inhibitor molecule. Figure 3.2.8 represents Nyquist plots of MS in 1 N HCl solutions without and at varied concentrations of AH extract. The significant changes were observed at varied concentrations of AH extract. The formation of semicircle slope is due to charge storage as a capacitor, which is discharged through resistor and also due to double layer behaviour (Hasyim et al., 2017). As seen from Figure 3.2.8, the diameter of capacitive loop increases with increase in concentration of inhibitor. This is an indication of decrease corrosion rate due to adsorption of inhibitor species like $H^+$ on the electrode surface (Bayol et al., 2008; Petek and Kovačič 2014). Similar trend was observed by Hoseizadeh et al (2014) and Umoren et al (2013).

The impedance diagrams (Nyquist plots) obtained show only one semicircle capacitance loop as seen from Figure 3.2.8. Semicircle shapes of Nyquist plots indicate charge transfer from metal surface during corrosion process. Impedance parameters, such as charge transfer resistance ($R_{ct}$), which is a measure of electron transfer across the surface and the double layer capacitance ($C_{dl}$) are obtained from the Nyquist plots in

Figure 3.2.8 (Muthukrishnan et al., 2015; Sethuraman et al., 2017). Fig. 3.2.8 also shows that $R_{ct}$ is directly proportional to the diameter of the capacitive loop and inversely proportional to the corrosion rate (Bammou et al., 2014). The decrease in $C_{dl}$ is related to increase in thickness of the double layer (Chaubey et al., 2015).

The value of $R_{ct}$was obtained by taking the difference of high and low frequency values of real impedance ($Z_{real}$). The changes of $R_{ct}$ and $C_{dl}$ values were attributed to the adsorption of inhibitor on the metal surface which decreases the extent of metal dissolution in corrosive medium (Karthik et al., 2015; Kumar et al., 2017). We noticed that the value of $R_{ct}$ increases as the diameter of Nyquist loop increases with increasing concentration of AH extract, however the $C_{dl}$ values decreases simultaneously.

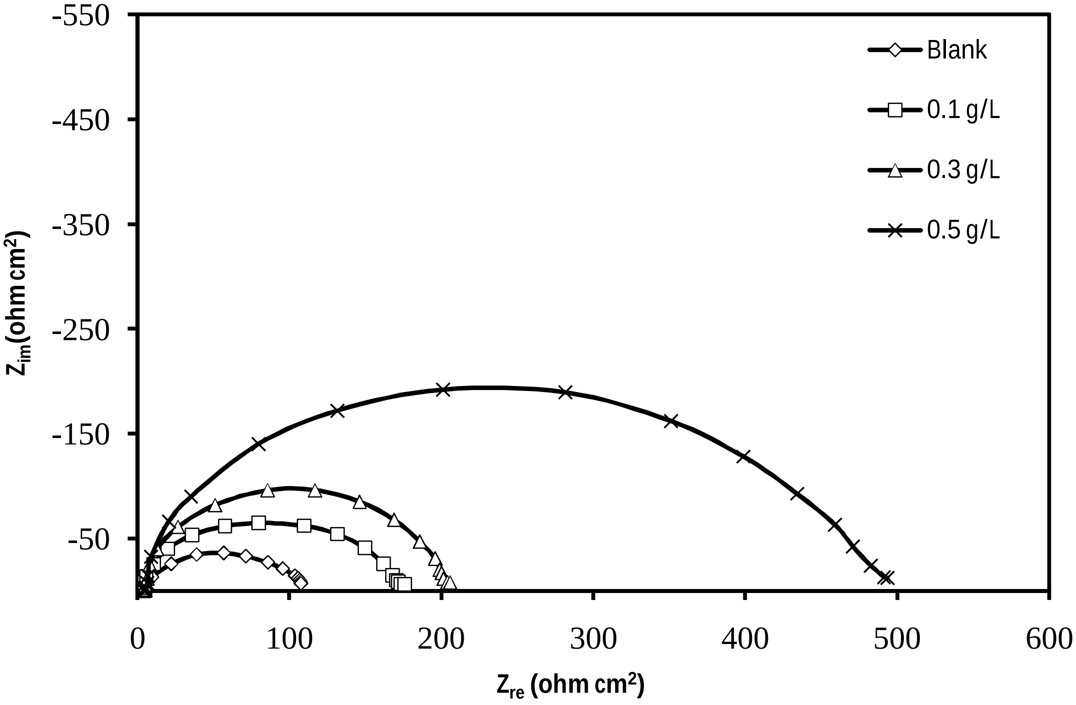


Figure 3.2.8: Nyquist plots for MS in 1 N HCl in presence and absence of different concentrations of AH extract.

The inhibition efficiency (%IE) was obtained from double layer capacitance ($C_{dl}$) followed by Dong et al (2011) method and listed in Table 3.2.6. Inspection of Table 3.2.6 shows that the $R_{ct}$ increases with increasing the concentration of inhibitor due to slower corrosion rate (Zhou et al., 2017). It is also observed from Table 3.2.6 that there is significant decrease in $C_{dl}$ on addition of inhibitor but the value increases with increasing inhibitor concentration. This result indicates that an increase in inhibitor concentration leads to the decrease in local dielectric constant or an increase in the thickness of the electrical double layer and suggests that the inhibitor molecules form a protective layer at the MS metal surface (Mobin et al., 2017).

Table 3.2.6: Corrosion parameters obtained from Nyquist plot from EIS measurement of MS in 1 N HCl without and with different concentration of AH extract.

| Conc. (g/L) | $R_s$ ($\Omega cm^2$) | $R_{ct}$($\Omega cm^2$) | $C_{dl}$ ($\mu F/cm^2$) | %IE |
|---|---|---|---|---|
| Blank | 4.01 | 103.96 | 386 | 00 |
| 0.1 | 4.57 | 171.43 | 116 | 69 |
| 0.3 | 4.15 | 201.76 | 50 | 86 |
| 0.5 | 4.4 | 489.49 | 20 | 94 |

These results indicate that inhibitor molecules adsorbed on metal surface and barrier between corrosive medium and metal surface (Yousefi et al., 2015). A similar trend was obtained from potentiodynamic polarization curves also (Li et al., 2016; Gupta et al., 2017). The increasing diameter of semicircle, which is to be characterized by the values of $R_{ct}$ (charge transfer resistance) with inhibitor concentration, indicates the formation of protective layer on metal surface.

### 3.2.4. FTIR of MS and AH extract

FT-IR spectrum of inhibitor and scratched surface of corrosion product with 0.5 g/L of AH extract after corroded medium were depicted in Figure 3.2.9. The main characteristic absorption bands appeared at 3389 $cm^{-1}$ as alcohol (–OH) and 2841 $cm^{-1}$ denoted symmetric methyl (–$CH_3$) stretching band. A characteristic band appeared at 1114 $cm^{-1}$ due to the ether band (C–O–C) and bands appeared at 1021 $cm^{-1}$is due to the carbon alcohol (C–OH) groups. In this figure also show the presence of sulphonate ester group ($SO_2$–O–) peak, which appeared at 1401 $cm^{-1}$ in the spectrum and this bond indicate sulphur hetroatom present in Allium species.

In the spectra of scratched surface of corrosion product with 0.5 g/L which is a change in intensity of band of some important functional groups. It is also observed that the asymmetric methyl group (-$CH_3$) stretching band at 2957 $cm^{-1}$ and thiol group (-SH) stretching band at 1401 $cm^{-1}$ are completely disappeared, while some bands such as -OH (3396 $cm^{-1}$), –C=O (1639 $cm^{-1}$) and C–C ring bending (606 $cm^{-1}$) shifted which may be due to adsorption of these functional groups on metal surface. This information indicates the presence of corrosion inhibitive functional groups containing hetero-atom and multiple bonds in AH extract, which block the active sites of MS surface.

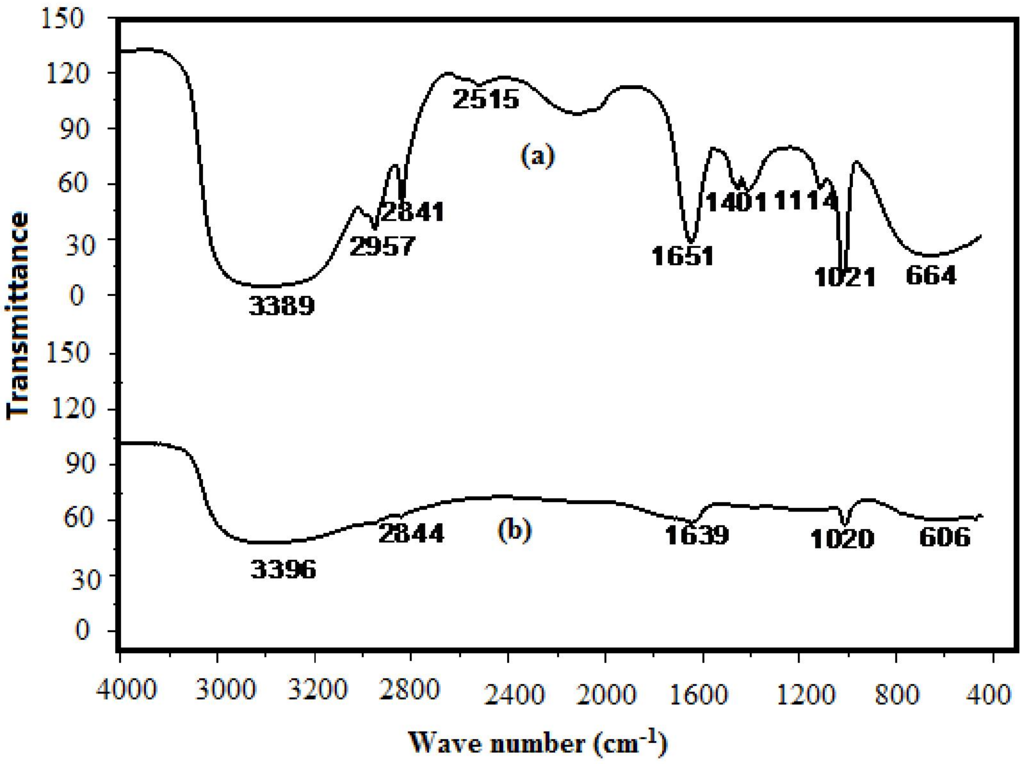


Figure 3.2.9: FT-IR spectra of (a) pure AH extract and (b) protective layer of MS after immersion for 3 h in acidic solution with 0.5 g/L of AH extract.

### 3.2.5. SEM of MS Surface

Microstructure study of MS surface in corrosive medium 1 N HCl was investigated in absence and presence of AH extracts at 300 K after 3-hour immersion. SEM images were obtained and results shown in Figure 3.2.10 (a-c). The clean surface obtained before immersion in test solution is shown in Figure 3.2.10 (a); it appears as a homogenous surface, Figure. 3.2.10 (b) exhibits the effect of 1 N HCl solution without inhibitor on the corrosion of MS at 300K. In the absence of inhibitor, a rough surface is observed (Figure 3.2.10(b). The metal surface is largely corroded as a result of the direct contact of MS surface with aggressive acidic solution resulted rough metal surface.

SEM image of the MS with addition of 0.5 g/L extract of AH, shows in Figure 3.2.10(c). The SEM image obtained with inhibitor is significantly different from the blank and without inhibitor in acidic solution. The cracked surface formed on metal surface is reduced, which indicates adsorptions of inhibitor molecule on metal surface and formation of protective layer. These observations were in good agreement with the result obtained from electrochemical measurements.

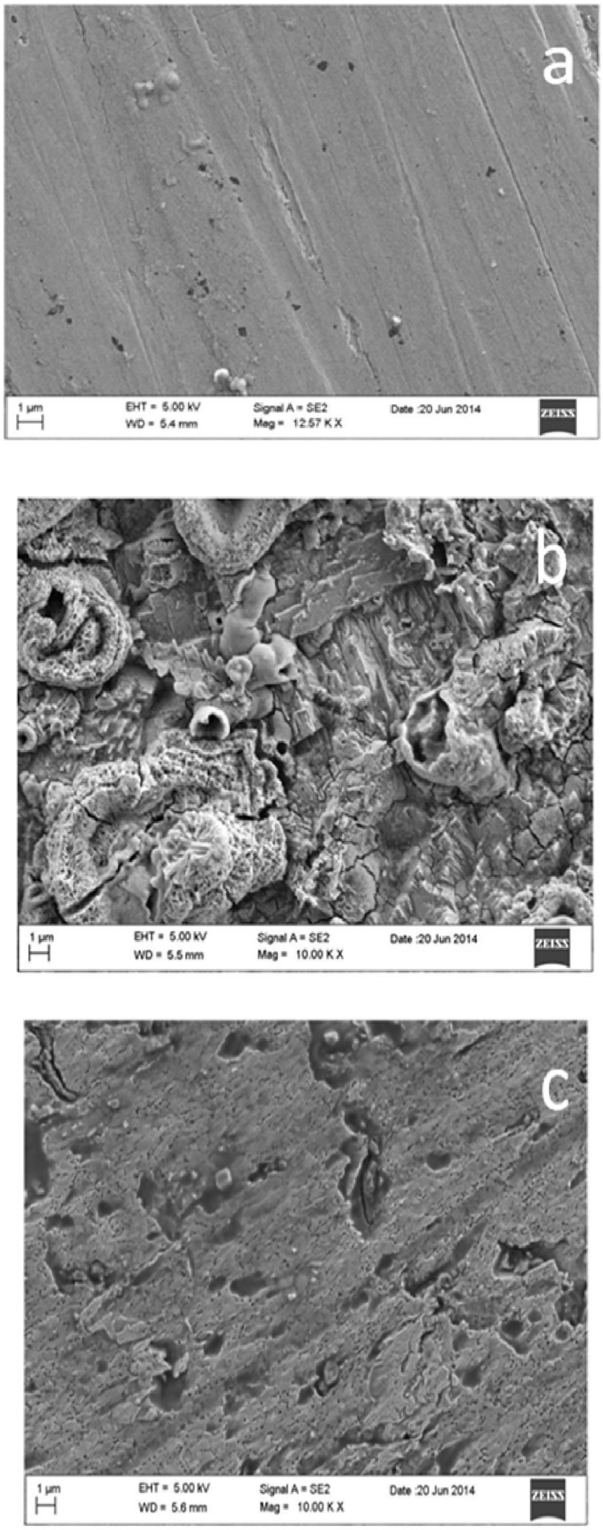


Figure 3.2.10: SEM image of MS specimen (a) before immersion in acid (b) after 3 h immersion without inhibitor (c) after 3 h immersion with the 0.5 g/L of AH.

### 3.2.6. Mechanism of Corrosion Inhibition of AH Extract

Figure 3.2.11 shows a probable inhibition mechanism due to adsorption of phytochemicals from AH extracts on MS surface (Guo et al., 2014). The interaction between organic molecules present in methanolic extract of AH is attributed as follows:

(i) Charge-transfer-type interaction between unshared electron pairs presents in oxygen in glucose derivative or π-electrons with empty low energy d- orbitals of Fe atom present on MS surface.

(ii) Columbic interactions between π-clouds and MS surface/solution interface or between protonated hydroxy and adsorbed $Cl^-$ ions at cathodic sides.

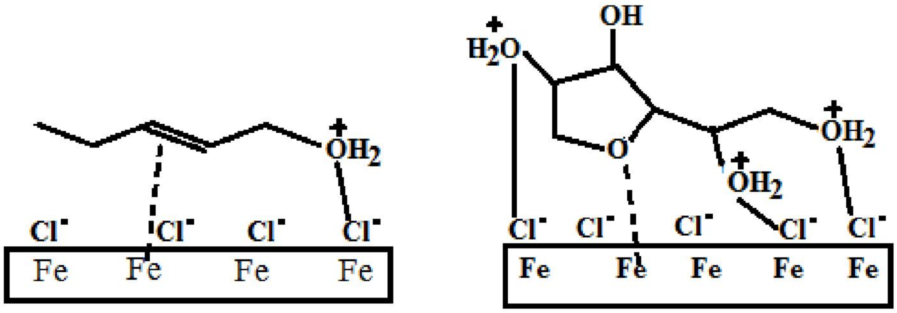


Figure 3.2.11: Schematic illustration of different modes of adsorption of AH extract on metal/acid interface.

## 3.3. Extract of Clerodendrum colebrookianum Walp Leaves (CCWL)

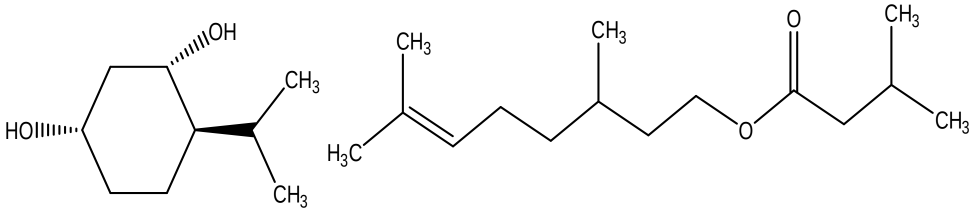
### 3.3.1. Phytochemical Analysis of CCWL by GC-MS

The use of plant extracts as green corrosion inhibitors has shown limitations of identification of active phytochemicals inhibiting the corrosion. However, the present work intended of screening the phytochemicals present with extract of CCWL using GC-MS. The GC-MS data obtained for the CCWL extract is presented in Table 3.3.1. The NIST reference was utilized for identification of various organic compounds present in the CCWL extract.

Table 3.3.1: Chemical constituents present in the CCWL extract using the GC-MS analysis.

| Hit | Rev | For | Compound name | M.W. | Formula | CAS |
|---|---|---|---|---|---|---|
| 1 | 918 | 803 | Phytol | 296 | $C_{20}H_{40}O$ | 150-86-7 |
| 2 | 890 | 753 | 3,7,11,15-tetramethyl-2-hexadecen-1-ol | 296 | $C_{20}H_{40}O$ | 102608-53-7 |
| 3 | 876 | 777 | Cyclohexanol, 1-methyl-4-(1-methylethyl) | 156 | $C_{10}H_{20}O$ | 21129-27-1 |
| 4 | 867 | 769 | Cyclohexanol, 5-methyl-2-(1-methylethyl)-, [1s-(1. alpha.2. alpha. 5. beta]. | 156 | $C_{10}H_{20}O$ | 2216-52-6 |
| 5 | 865 | 755 | Cyclohexanol, 5-methyl-2-(1-methylethyl)-, [1r-(1. alpha. 2. beta., 5. alpha]. | 156 | $C_{10}H_{20}O$ | 2216-51-5 |
| 6 | 865 | 776 | Cyclohexanol, 5-methyl-2-(1-methylethyl)-, [1s-(1. alpha.2. alpha. 5. beta]. | 156 | $C_{10}H_{20}O$ | 2216-52-6 |
| 7 | 859 | 778 | Cyclohexanol, 5-methyl-2-(1-methylethyl)-, (1. alpha.2. beta. 5. alpha)- | 156 | $C_{10}H_{20}O$ | 89-78-1 |
| 8 | 859 | 746 | 2,6,10-trimethylundeca-1,3-diene | 194 | $C_{14}H_{26}$ | 900222-09-1 |
| 9 | 858 | 698 | Phytol | 296 | $C_{20}H_{40}O$ | 150-86-7 |
| 10 | 858 | 761 | Cyclohexanol, 5-methyl-2-(1-methylethyl)-, [1s-(1. alpha. 2. beta., 5. beta)] | 156 | $C_{10}H_{20}O$ | 23283-97-8 |
| 11 | 853 | 737 | 6-octen-1-ol, 3,7-dimethyl | 156 | $C_{10}H_{20}O$ | 26489-01-0 |
| 12 | 851 | 755 | Cyclohexanol, 5-methyl-2-(1-methylethyl)-, (1. alpha. 2. beta.,5. alpha) | 156 | $C_{10}H_{20}O$ | 15356-70-4 |
| 13 | 850 | 754 | Oxirane, tetradecyl | 240 | $C_{16}H_{32}O$ | 7320-37-8 |
| 14 | 850 | 746 | Butanoic acid, 3,7-dimethyl-6-octenyl ester | 226 | $C_{14}H_{26}O_2$ | 141-16-2 |
| 15 | 849 | 734 | Cyclohexanol, 5-methyl-2-(1-methylethyl)-, (1. alpha. 2. beta., 5. beta) | 156 | $C_{10}H_{20}O$ | 490-99-3 |
| 16 | 848 | 743 | Cyclohexanol, 5-methyl-2-(1-methylethyl)-, [1s-(1. alpha. 2. beta., 5. beta)] | 156 | $C_{10}H_{20}O$ | 23283-97-8 |
| 17 | 847 | 733 | Cyclohexanol, 5-methyl-2-(1-methylethyl)-, (1. alpha. 2. alpha., 5. alpha)- | 156 | $C_{10}H_{20}O$ | 491-02-1 |
| 18 | 846 | 748 | Cyclohexanol, 5-methyl-2-(1-methylethyl)-, (1. alpha. 2. beta., 5. beta)- | 156 | $C_{10}H_{20}O$ | 490-99-3 |
| 19 | 845 | 707 | Phytol | 296 | $C_{20}H_{40}O$ | 150-86-7 |
| 20 | 843 | 723 | 2-octen-1-ol, 3,7-dimethyl | 156 | $C_{10}H_{20}O$ | 40607-48-5 |

It is difficult to find a standard sample to analyse these complex structures in sequentially. However, the GC-MS spectra along with the NIST library database (Marimuthuet al., 2013) revealed the presence of major components as cyclohexanol derivative, 3, 7, 11, 15-tetramethyl-2-hexadecen-1-ol, butanoic acid, 3, 7-dimethyl-6-octenyl ester and phytol (Figure 3.3.1).



1-methyl-4-propan-2-cyclohexan-ol

3,7-dimethyl-6-octenyl-butanoate

Figure 3.3.1: Main phytochemical constituents in CCWL extract.

## 3.3.2. Gravimetric Measurements of CCWL Extract

### 3.3.2.1. Effect of CCWL Concentration

Table 3.3.2 illustrates that a rapid decrease in corrosion rate was recorded by increasing the inhibitor concentrations. This is due to fact that more inhibitor molecules are adsorbed over MS surfaces and hence, adsorption coverage increases with increasing the concentration of inhibitor. This eventually protects the MS surface from aggressive acidic corrosion medium. It is also noted from Table 3.3.2 that surface coverage (θ) is increased with an increase in inhibitor concentration at working temperature of 303 K. Similar trends were observed by Li et al (2012) in their study of inhibition efficiency of bamboo leaves in HCl and $H_3PO_4$ acids. The corrosion rate of MS in 1 N HCl was observed as 3.25 mg/cm$^2$/h which were decreased to 0.15 mg/cm$^2$/h in presence of 0.4 g/L of CCWL extract with 95% surface coverage over MS. Thus, it is clear from the results that the decrease in corrosion rate in the corrosive medium is due to the formation of protective films over the MS surface in presence of inhibitor molecules (Abboud et al., 2009). Inhibitive action of the extract of Eucalyptus globules was reported by Tezeghdent et al (2015). It was further reported that eucalyptol was a probable inhibitive molecule present in Eucalyptus globules extract. Table 3.3.2 further reveals that the inhibition efficiency is increased linearly with increasing the concentration of plant extract. Similarly, the corrosion rate is decreased at higher inhibitor concentrations (Figure 3.3.2). Similar results were reported for Occimum viridi extract.

Table 3.3.2: Gravimetric analysis for MS in 1 N HCl at 303 K in absence and presence of various concentrations of CCWL extract.

| Conc.(g/L) | $C_{rate}$ (mg/cm$^2$/h) | %IE | θ |
|---|---|---|---|
| Blank | 3.25 | 00 | 00 |
| 0.1 | 0.54 | 83.2 | 0.83 |
| 0.2 | 0.40 | 87.4 | 0.87 |
| 0.4 | 0.15 | 95.2 | 0.95 |

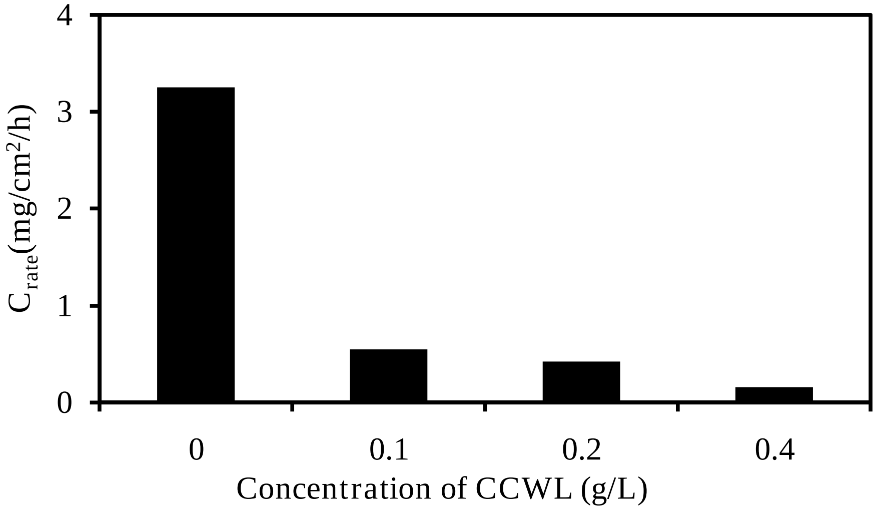


Figure 3.3.2: Variation of corrosion rate with different concentration of CCWL extract.

### 3.3.2.2. Effect of Temperature of CCWL Extract

The temperature effect on corrosion inhibition efficiency of MS sheet in 1N HCl was evaluated using the weight loss method at different temperatures (303 K – 333 K) and in absence and presence of CCWL extracts. The values of $C_{rate}$ are determined by gravimetric method at different temperatures in presence of 0.4 g/L CCWL extract and results are illustrated in Figure 3.3.3.

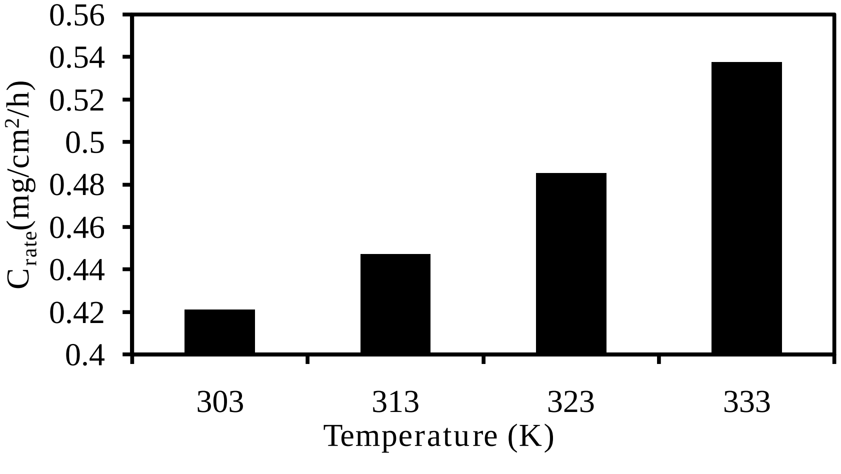


Figure 3.3.3: Variation of corrosion rate of MS at different temperatures in presence of 0.4 g/L concentration CCWL extract.

It is noticed from Figure 3.3.3 that the corrosion rate for MS at 0.4 g/L CCWL concentration in 1 N HCl is increased by raising the temperature from 303 K to 333K. The increase in corrosion rate is due to decrease in adsorption of CCWL extract on MS sheet with an increase in temperature. The inhibitor molecules diffuse into solution from MS surface with an increase in temperature and hence, more surface area of MS is exposed to acidic medium, which results in decrease of %IE. An equilibrium may be established between adsorption and desorption process in presence of inhibitors.

### 3.3.2.3. Adsorption isotherm of CCWL Extract

A linear relationship between $C_{inh}/\theta$ and concentration of CCWL extract with a correlation coefficient value ($R^2>0.99$) is presented in Figure 3.3.4. This suggests that the adsorption of CCWL extract onto the MS surface followed Langmuir's adsorption isotherm (Li et al., 2010). The values of $K_{ads}$ were found to decrease with increase in temperature and therefore, it is interpreted that the interaction between inhibitor molecules with metal surface is favourable at lower temperatures.

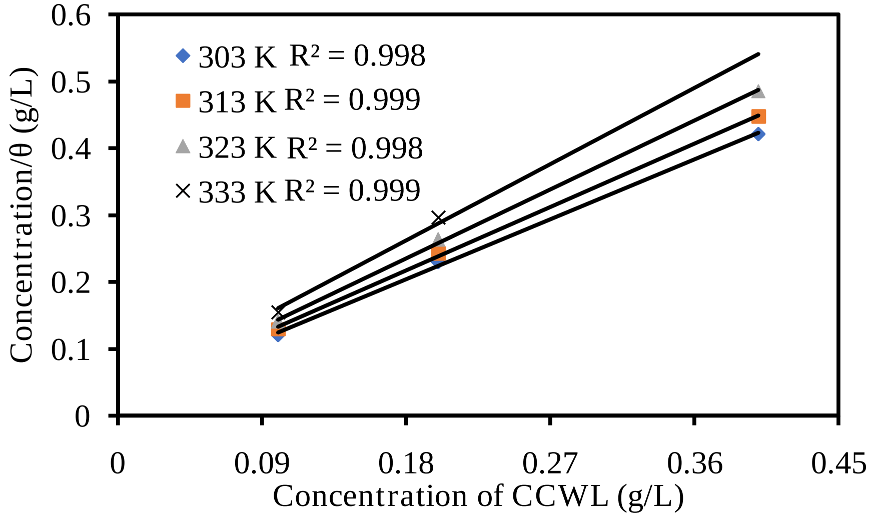


Figure 3.3.4: Langmuir adsorption isotherm in presence of CCWL extract for MS in 1 N HCl.

This finding also suggests that the physical adsorption of inhibitor took place onto the MS sheet. The corresponding value of standard adsorption free energy is found between -26.69 to -28.45 kJ/mol, which is suggests that the adsorption of CCWL extract over the MS surface is physisorption by the electrostatic interactions between the inhibitor molecules and the charged metal surface (Obi-Egbedi and Obot, 2013). Further the negative values of free energy of adsorption indicate the spontaneous process of adsorption. It is worth to mention here that the other isotherms are not tested. The lower value of adsorption equilibrium constant also attributes to the, possible, weak interaction force that holds the inhibitor molecules on metal surface and inhibition process exhibited by physisorption.

Further, the understanding of corrosion inhibition was demonstrated with the help of Arrhenius plots (Figure 3.3.5) and Transition-state plots (Figure 3.3.6), respectively. The thermodynamic parameters (Table 3.3.3) showed the positive value of $\Delta H_a$ which indicated the corrosion process is endothermic in nature, while a negative correlation is found between the values of $\Delta S_a$ in corrosive medium.

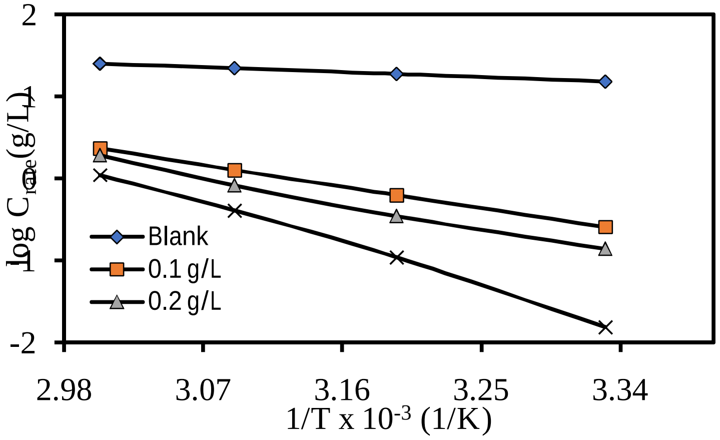


Figure 3.3.5: Arrhenius plots for MS corrosion rates versus 1/T in 1 N HCl in presence and absence of CCWL extracts.

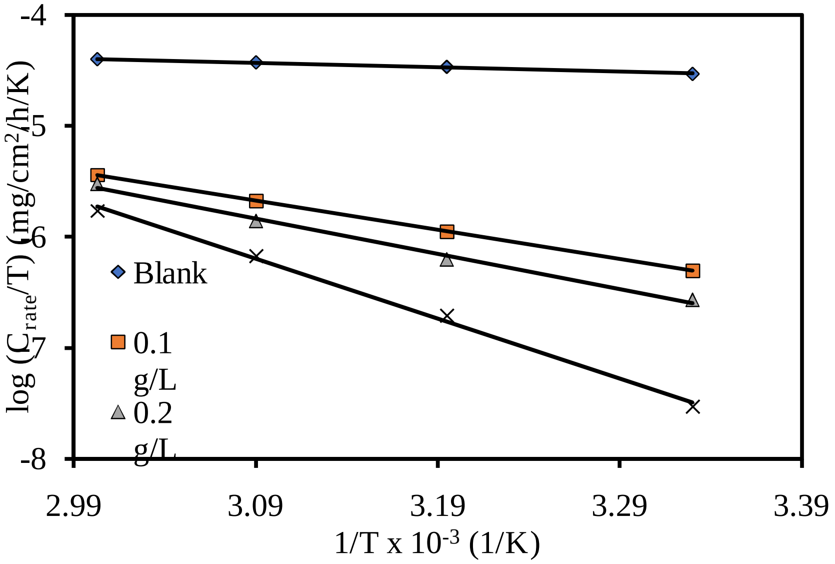


Figure 3.3.6: Transition-state plots for MS corrosion rates in 1 N HCl in absence and presence of various concentrations of CCWL extracts.

Table 3.3.3: Thermodynamic parameters for MS in acidic medium in various concentration of CCWL extract at a temperature range (303 K -333 K).

| Conc.(g/L) | $E_a$(kJ/mol) | $\Delta H_a$(kJ/mol) | -$\Delta S_a$(J/mol/K) |
|---|---|---|---|
| Blank | 06.279 | 03.630 | 223.180 |
| 0.1 | 26.700 | 24.060 | 170.398 |
| 0.2 | 31.84 | 29.200 | 155.87 |
| 0.4 | 51.82 | 49.187 | 97.12 |

### 3.3.3. Electrochemical Measurements of CCWL extract

#### 3.3.3.1. Measurement of Potentiodynamic Polarization of CCWL extract

Figure 3.3.7, shows the potentiodynamic polarization behaviour of MS in 1 N HCl solution without and with different concentrations of CCWL extract (0.1 g/L - 0.4 g/L) at temperature 303 K. For this study, the MS coupons were exposed to test solutions for 3 h with suitable arrangement of electrode. It can be observed from the polarization curves that $I_{corr}$ decreases with increasing concentration of CCWL extract in acidic media. The change of cathodic and anodic Tafel slopes in blank and in the presence of different concentrations of the inhibitor was also compared. This result indicates that the CCWL extract suppressed both the anodic and cathodic reactions (Prabakaran et al., 2016).

Inspection of the Figure 3.3.7 and Table 3.3.4 reveals that the corrosion potential shifted towards negative value and cathodic curves shifted towards lower current densities in presence of plant extract as compare to blank. This may be due to adsorption of inhibitor extract over the cathodic active corrode surface and decrease the corrosion rate. It is also observed that the anodic reaction is more dominant with increasing concentration of inhibitor (higher value of $ß_a$ over $ß_c$). It means that the anodic reaction is predominant (Montemor, 2016). This observed phenomenon indicates that inhibitor could suppress the dissolution of iron whereas the variation of cathodic Tafel slope suggests that the suppression of the hydrogen evaluation reaction by CCWL extract (Yadav et al., 2013).

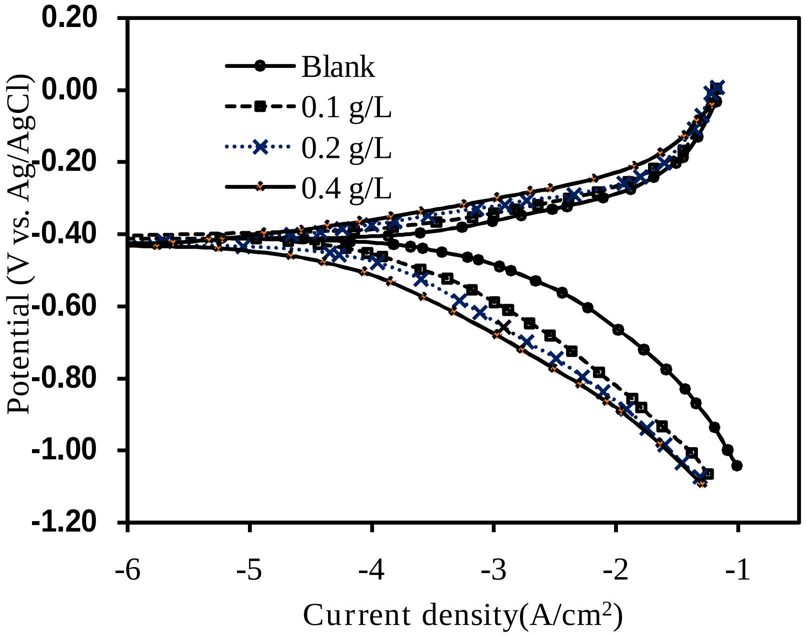


Figure 3.3.7: Polarisation curves for MS in 1N HCl in absence and presence of different concentrations of CCWL extract at 303 K.

Table 3.3.4: Electrochemical parameter obtained from low carbon steel in 1N HCl in absence and presence of different concentrations of CCWL extract at 303 K.

| Conc. (g/L) | $-E_{corr}$(mV vs Ag/AgCl | $I_{corr}$ (μA/cm$^2$) | %IE | $R_{ct}$ (Ωcm$^2$) | $C_{dl}$ (μF/cm$^2$) | %IE |
|---|---|---|---|---|---|---|
| Blank | 396 | 446.93 | 00.00 | 124.14 | 2801.0 | 00.00 |
| 0.1 | 424 | 82.80 | 81.45 | 691.74 | 566.0 | 82.05 |
| 0.2 | 422 | 49.43 | 88.94 | 752.71 | 546.0 | 83.5 |
| 0.4 | 407 | 22.50 | 94.96 | 1092.47 | 419.0 | 88.6 |

From Table 3.3.4, it can be seen that the corrosion current density is significantly decreased from 446.93 µA/cm$^2$ to 22.507 µA/cm$^2$ and increase of corrosion inhibition efficiency (%IE) from 81.45 to 94.96 with increasing concentration of inhibitor form 0.1 g/L to 0.4 g/L. The similar results have been reported with other corrosion inhibitor (Martinez,2003; Behpour et al., 2011).

### 3.3.3.2. EIS of CCWL extract

EIS is one of the most important tools for monitoring electrochemical interaction between electrode and electrolyte. Figure 3.3.8 represents Nyquist plots of MS in 1 N HCl solutions without and with different concentrations of CCWL extract. The significant impedance change was observed on addition CCWL extract. The formation of semicircle is due to charge storage as a capacitor, which is discharged through resistor as well as double layer behaviour of MS (Meng et al., 2017).

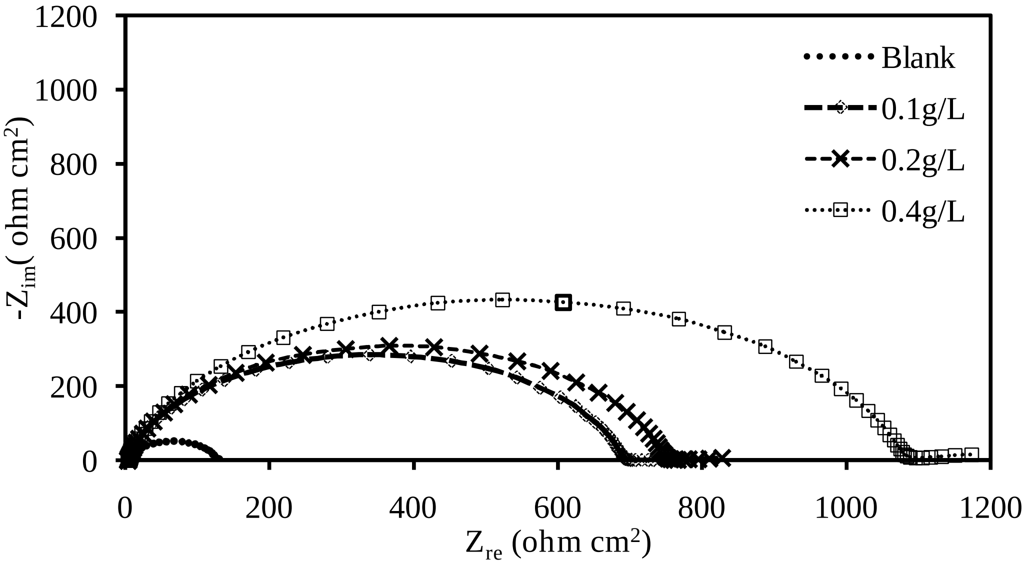


Figure 3.3.8: Nyquist plot for MS in acidic solution in absence and presence of various concentration of CCWL extract.

As seen from Figure 3.3.8, the diameter of capacitive loop increases with an increase in inhibitor concentration. This is an indication of decrease corrosion rate due to adsorption of inhibitor species or species like $H^+$ on the electrode surface (Noor, 2009). Similar trend was observed by Garai et al (2012) and Nataraja et al (2011). Further, the Nyquist plots show that only one semicircle capacitance loop is seen (Cf Figure 3.2.8) and semicircle shapes of Nyquist plots indicate charge transfer occurred during the corrosion process.

Inspection of Table 3.3.4 shows that the $R_{ct}$ increases with an increase in concentration of inhibitor which is due to slower corrosion rate (Ramírez-Estrada et al., 2017) and at the highest concentration of inhibitor; the inhibition efficiency is found to maximum. It is also observed from Table 3.3.4, that there is significant decrease in $C_{dl}$ onaddition of inhibitor. This result indicates that an increase in inhibitor concentration leads to decrease the local dielectric constant or an increase in the thickness of the electrical double layer and suggests that the inhibitor molecules form a protective layer at the MS surface.

### 3.3.4. FT-IR of MS and CCWL Extract

The formation of protective layer over MS surface was confirmed by the FT-IR spectra of CCWL extract. FT-IR analysis for pure extract and corrosive compound are presented in Figure 3.3.9. The spectrum of CCWL extract shows the presence of -OH at vibration band of 3380 $cm^{-1}$. However, on the CCWL covered MS surface showed that this band was shifted to 3353 $cm^{-1}$. The low intensity of broad peak at 3353 $cm^{-1}$ indicates an interaction between the free –OH with charged metal surface. A characteristic peak at 629 $cm^{-1}$ is attributed to the metal-oxygen (functional group) bond.

Moreover, peak at 2124 $cm^{-1}$is mainly attributed to the −C≡C-H (terminal alkyne) and the disappearance of this peak indicates that the π-electrons of inhibitor molecules are also being involved in bonding on the metal surface. These shifting in the absorption frequencies clearly indicate that one or more phytochemicals of inhibitor are adsorbed over the MS surface (El-Etre et al., 2005; Ostovari et al., 2009).

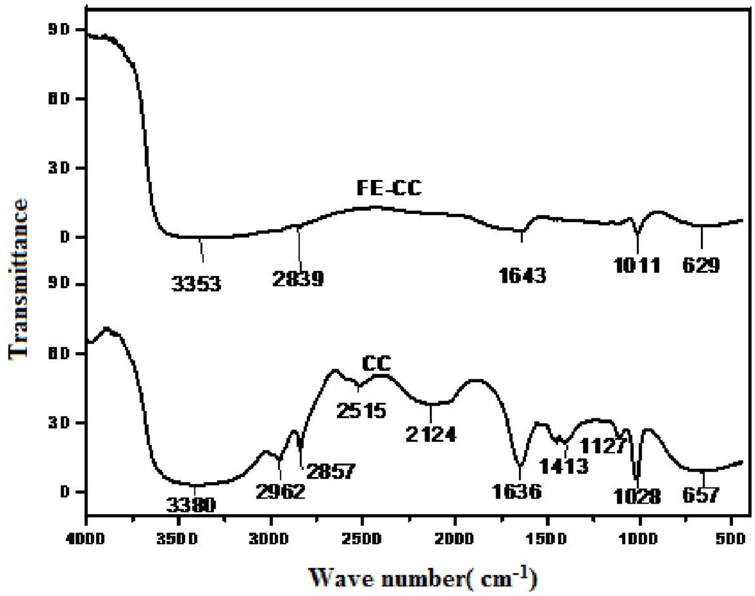


Figure 3.3.9: FT-IR spectra of (CC) pure CCWL extract and (FE-CC) protective layer developed on MS after immersion in 1 N HCl containing 0.4 g/L of CCWL extracts for 3h.

### 3.3.5. SEM of MS Surface

Figure 3.3.10(a-c) shows SEM images of the surface of MS before immersion and after immersion in 1 N HCl without and with 0.4g/L of CCWL extract for 3 h respectively. Figure 3.3.10(b) shows rough and cracked surface of MS in the absence of inhibitor due to metal dissolution in corrosive medium. A significant change on MS surface is observed from Figure 3.3.10(c) with 0.4g/L CCWL extracts. The dissolution of metal in corrosive medium is considerably minimized and the smooth surfaces is appeared possibly due to uniform formation of a protective film on the metal surface compared to the polished surface shown in Figure 3.3.10(a) (Li et al., 2015). Hence, from the present study, it is concluded that the corrosion of metal was strongly inhibited by CCWL extract in 1 N HCl.

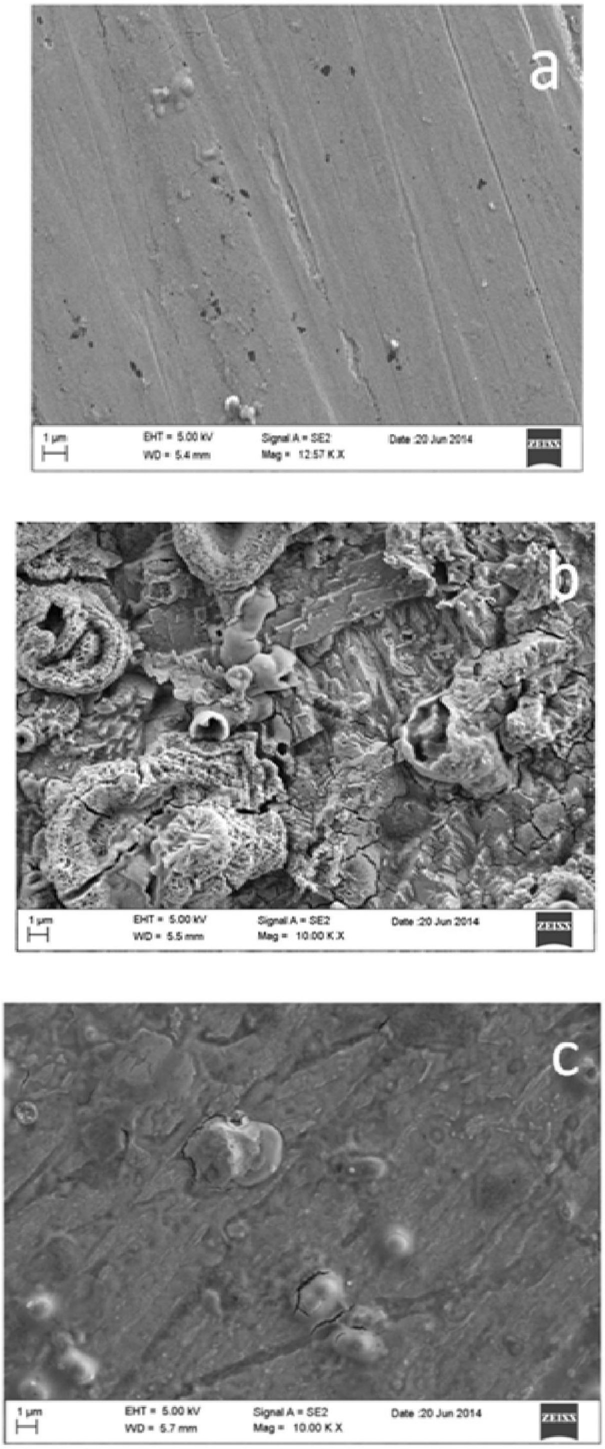


Figure 3.3.10: SEM images of MS: (a) before immersion in corrosive solution; (b) after immersion in 1 N HCl for 3 h and (c) after immersion in 1N HCl solution containing 0.4 g/L of CCWL extract for 3 h.

### 3.3.6. Mechanism of Corrosion Inhibition of CCWL Extract

The adsorption of inhibitor molecules on the surface of MS is having two steps process: (i) diffusion of inhibitor molecules from aqueous phase to double layer and (ii) adsorption of inhibitor over MS surface. The results obtained from GC-MS studies show the presence of various types of organic compounds present in the CCWL extract. The inhibitive action of CCWL extract on MS in corroding medium is attributed to the adsorption of these components, viz., cyclohaxanol derivative containing oxygen atoms in functional groups (-OH) and butanoic acid through C=C. A molecule of small size as cyclohexanol derivative is diffused rapidly and covered the MS surface.

In acidic medium, these compounds may exist as protonated species, which interact with $Cl^-$ on metallic surface (Figure 3.3.11). Potentiodynamic polarisation curves indicate that these inhibitor molecules retarded the corrosion by controlling both anodic and cathodic reactions. Protonated molecules adsorb on cathodic sites of MS to retard $H_2$evolution process, whereas π-system adsorb on anodic sites of MS to prevent the diffusion of metal ions into aqueous phase (Yadav et al., 2015).

Proposed adsorption mechanism is indicatively understood by the FT-IR study discussed as above. FT-IR spectroscopy analysis (Figure 3.3.9) also reveals that the shifting in peaks of –OH and C=C vibration is due to physical interaction between charged metal surface with protonated cyclohexanol and butanoic acid.

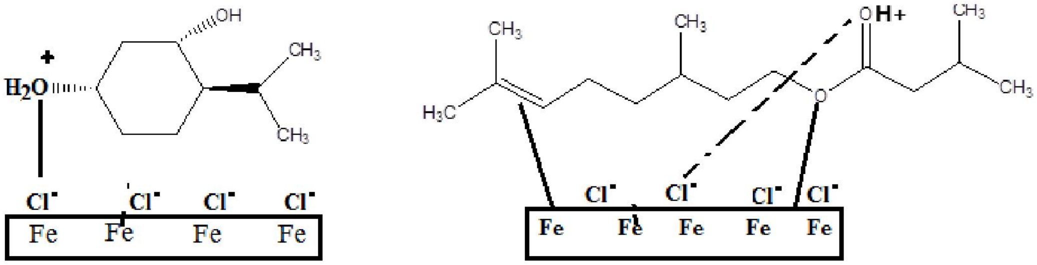


Figure 3.3.11: Schematic corrosion inhibition mechanism of main constituents compounds in crude CCWL extract.

## 3.4. Extract of Elsholtzia communis Inflorescence (ECI)

### 3.4.1. Phytochemical Analysis of ECI extract by GC-MS

The data obtained from the GC-MS analysis of the ECI extract is shown in Table 3.4.1 with their molecular weight. The results of GC-MS are obtained by measuring the peak area using Turbo Mass software and matched with the NIST standard library. In view of corrosion inhibition study, structures of few organic molecules are presented in Figure 3.4.1.

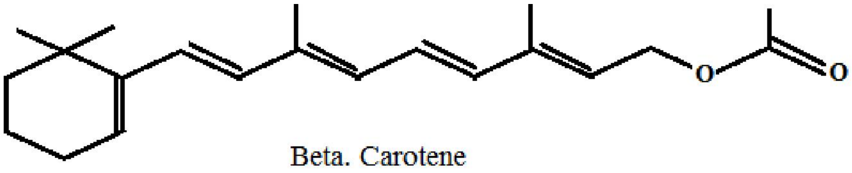


Figure 3.4.1: Main phytochemical constituents in ECI extract.

The major phytochemicals present in ECI extract are β carotene, retinoic acid and retinol acetate as carotenoids derivatives. Recently, Mourya et al (2014) also reported the corrosion inhibition effect of the carotenoid derivatives. A combined GC-MS spectral data analysis reveals that the phytochemical constituents of ECI extract have potential to inhibit the acid corrosion of MS due to presence of hetero atoms and π-bonds in β carotene, retinoic acid and retinol acetate.

Table 3.4.1: Chemical constituents present in the ECI extract using the GC-MS analysis.

| Hit | Rev | for | Compound Name | M. W. | Formula | CAS |
|---|---|---|---|---|---|---|
| 1 | 757 | 578 | Cholesta-8, 24-Dien-3-OL, 4-Methyl-, (3. Beta, 4. alpha.) | 398 | $C_{28}H_{46}O$ | 7199-92-0 |
| 2 | 728 | 532 | 6,10-dodecadien-1-yn-3-ol, 3,7,11-Trimethyl | 220 | $C_{15}H_{24}O$ | 2387-68-0 |
| 3 | 727 | 529 | Stigmastan-6,22-Dien,3,5-Dedihydro | 394 | $C_{29}H_{46}$ | 107304-12-1 |
| 4 | 727 | 539 | 17-(1,5-dimethylhexyl)-10,13-dimethyl-1,7,8,9,10,11,12,13,14,15,16,17-Dodeca | 382 | $C_{27}H_{42}O$ | 24116-50-5 |
| 5 | 723 | 542 | Beta. Carotene | 536 | $C_{40}H_{56}$ | 7235-40-7 |
| 6 | 718 | 508 | Retinoic Acid | 300 | $C_{20}H_{28}O_2$ | 302-79-4 |
| 7 | 716 | 523 | Cholesta-6,22,24-Triene,4,4-dimethyl | 394 | $C_{29}H_{46}$ | 900128-66-9 |
| 8 | 711 | 504 | Retinol Acetate | 328 | $C_{22}H_{32}O_2$ | 127-47-9 |
| 9 | 709 | 559 | Trans-Z-. Alpha. -Bisabolene Epoxide | 220 | $C_{15}H_{24}O$ | 900131-71-1 |
| 10 | 708 | 528 | Kryptogenin 2,4-Dinitro Phenyl Hydrazone | 790 | $C_{39}H_{50}O_{10}N_8$ | 900253-58-5 |
| 11 | 705 | 495 | 8A(2H)-phenanthrenol,7-Ethenyl Dodecahydro-1,1,4A,7-Tetramethyl | 332 | $C_{22}H_{36}O_2$ | 41756-14-3 |
| 12 | 693 | 495 | Kauren-18-ol, Acetate, (4. beta.) | 330 | $C_{22}H_{34}O_2$ | 72150-74-4 |
| 13 | 692 | 468 | Beta. Carotene | 536 | $C_{40}H_{56}$ | 7235-40-7 |
| 14 | 690 | 512 | Olean-12-en-28-al, Cyclic 1,2-Ethanediyl Mercaptal | 500 | $C_{32}H_{52}S_2$ | 54446-81-0 |
| 15 | 689 | 478 | 26-hydroxy Cholesterol | 402 | $C_{27}H_{46}O_2$ | 13095-61-9 |
| 16 | 686 | 476 | StigmasterylTosylate | 566 | $C_{36}H_{54}O_3S$ | 53139-42-7 |
| 17 | 674 | 529 | Pentacyclo[9.1.0.0(2,4).0(5,7).0(8,10)]Dodecane, 3,3,6,6,9,9,12,12-Octamethyl | 272 | $C_{20}H_{32}$ | 75349-96-1 |
| 18 | 659 | 508 | 2-hydroxy-1,1,10-Trimethyl-6,9-Epidioxy-7-Octalin | 224 | $C_{13}H_{20}O_3$ | 108511-80-4 |
| 19 | 657 | 451 | Beta. Carotene | 536 | $C_{40}H_{56}$ | 7235-40-7 |
| 20 | 653 | 504 | (-)-Spathulenol | 220 | $C_{15}H_{24}O$ | 77171-55-2 |

### 3.4.2. Gravimetric Measurements of ECI Extract

#### 3.4.2.1. Effect of ECI extracts concentration

The weight loss measurements are presented in Table 3.4.2. This illustrates the effect of ECI extract on the $C_{rate}$ and the %IE. It is further observed that there is a significant and gradual decrease in $C_{rate}$ as the concentration of ECI extract is increased. However, the values of the %IE and q are increased with inhibitor concentration (Adejoro et al., 2015; Nwankwo et al., 2017). This is due to increase in the extent of adsorption of inhibitors from ECI extract onto the MS surface in 1 N HCl medium.

Table 3.4.2: Gravimetric analysis for MS in 1 N HCl at 300 K in absence and presence of various concentrations of ECI extract.

| Conc.(g/L) | $C_{rate}$ (mg/cm$^2$/h) | %IE | θ |
|---|---|---|---|
| Blank | 5.87 | 00 | 0.00 |
| 0.1 | 3.17 | 45 | 0.45 |
| 0.3 | 1.11 | 81 | 0.81 |
| 0.5 | 0.51 | 91 | 0.91 |

#### 3.4.2.2. Effect of Temperature

The temperature accelerates hydrogen evolution reaction on metal surface in acidic medium hence, the corrosion rate increases. This results in decrease of %IE at higher temperature and it is attributed to desorption of the inhibitor molecules from the MS surface and an increase in area of metal surface exposed to corrosive acidic medium.

A decrease in the adsorption of ECI extract on metal surface at higher temperature is primarily the reason of increased corrosive process of the metal.

The adsorption of inhibitors on the metal surface depends on the structure and electronic properties of inhibitor molecules, electrochemical potentials at the interface of metal-corrosive solution and the temperature of corrosive medium itself. The effect of temperature on the corrosion rate and inhibition efficiency of ECI extracts for MS corrosion in 1 N HCl was studied using weight loss methods and presented in table 3.4.2. It is observed from the Figure 3.4.2 that the inhibition efficiency decreases with increase in temperature; however, corrosion rate increases with rise in temperature at all studied concentration of ECI extract.

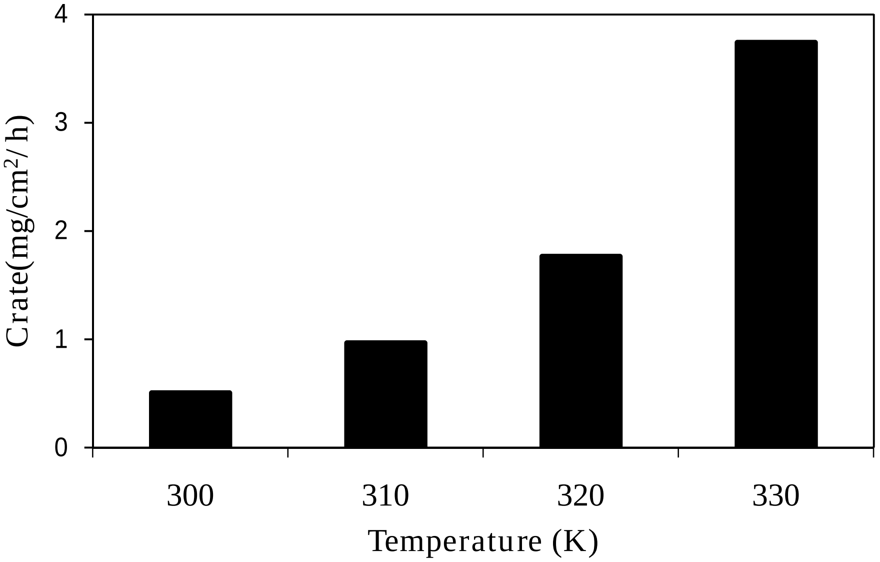


Figure 3.4.2: Variation of corrosion rate with 0.5g/L of ECI extract in 1 N HCl at various temperature.

### 3.4.2.3. Adsorption Isotherm of ECI Extract

The inhibition mechanism of inhibitors is estimated by the θ values, which has been determined from gravimetric analysis at different concentrations of ECI extracts and the same has been reported in Table 3.4.2. The $C_{inh}/\theta$ versus $C_{inh}$ was plotted and shown in Figure 3.4.3. A linear relationship between $C_{inh}/\theta$ and $I_{nhi}$ving a correlation coefficient ($R^2$) of 0.99 is obtained. This suggests that the adsorption of ECI on the MS surface obeyed Langmuir's adsorption isotherm. Thus, the adsorption of inhibitor on the MS surface is assumed to be monolayer with no lateral interaction between the adsorbed molecules, even on adjacent sites (Ating et al., 2010). The values of $K_{ads}$ at 0.1, 0.3 and 0.5 g/L of ECI extract were calculated from the intercept of corresponding straight lines in Figure 3.4.3.

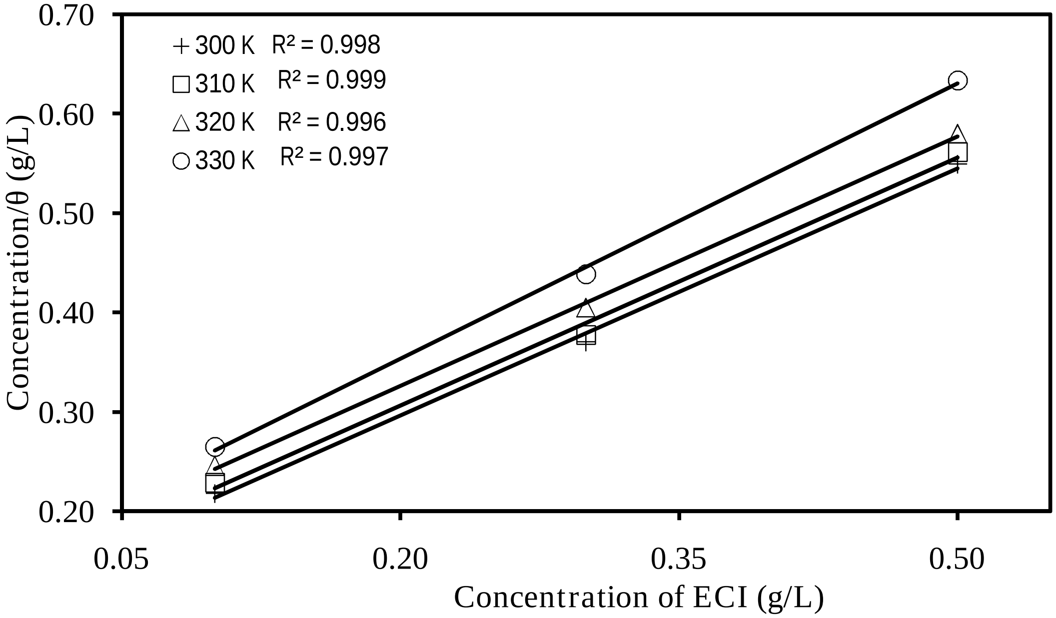


Figure 3.4.3: Langmuir adsorption isotherm plots for MS in 1 N HCl solutions in the presence of various concentrations of ECI extract at different temperature.

The obtained value of standard free energy of adsorption in presence of ECI extracts at different concentrations (0.1, 0.3 and 0.5 g/L) and temperatures (300 K- 330 K) presented in Table 3.4.3 and found around -15 kJ/mol. Generally, the less negative value of standard free energy of adsorption around (–20 kJ/mol) are usually characteristic of physical adsorption whereas more negative value (–40 kJ/mol) is associated with charge transfer or sharing of electrons. However, such adsorptions were not concluded as purely physical or chemical in nature. The lower values of standard free energy obtained in this system is concluded as intense physisorption of ECI extract on MS surface at all studied temperatures and concentrations (Saha et al., 2016; Raghavendra and Bhat, 2016). Further the adsorption constant as obtained by weight loss measurements in presence of ECI extract at different concentrations (0.1 g/L – 0.5 g/L) and temperatures (300 K- 330 K) are presented in Table 3.4.3.

Table 3.4.3: Calculated values of adsorption isotherm adsorption and standard free energy for the adsorption of ECI extract on MS surface in 1 N HCl solution at different temperatures.

| Temp.(K) | -$\Delta$ (kJ/mol) | $K_{ads}$ |
|---|---|---|
| 300 | 15.08 | 7.64 |
| 310 | 15.48 | 7.33 |
| 320 | 15.62 | 6.40 |
| 330 | 15.86 | 5.84 |

Mourya et al (2014) reported the inhibition efficiency of Marigold flower extract (0.5g/L) decreases from 99.8 % to 40.0 % with a rise in temperature from 293 K to 333 K. This comparative study concludes that the Marigold flower extract is a good inhibitor only at lower concentrations and temperatures whereas ECI extract shows good inhibition efficiency even at higher temperatures. This study also supports the physical adsorption of inhibitor molecules on metal surface. It is apparent from Figure 3.4.3 that at a particular concentration of ECI extract, %IE decreases with an increase in temperature from 300 to 330 K. It is known that the physisorption is favourable at lower temperature due to the low heat of adsorption whereas chemisorption is favourable at higher temperatures because of high adsorption energy (Rahiman and Sethumanickam, 2017).

Figure 3.4.4 shows the plots of log $C_{rate}$ versus 1/T for blank and at all concentrations of ECI extract, which gave straight lines. The values of $E_a$ were obtained from the slops of these straight lines and listed in Table 3.4.4. The higher value of $E_a$ in presence of ECI extract solutions suggests that (i) physical adsorption of inhibitor molecules onto the MS surface, (ii) concentration dependent inhibition performance and (iii) formation of a physical barrier at MS surface/solution interface (Hamdy and El-Gendy, 2013).

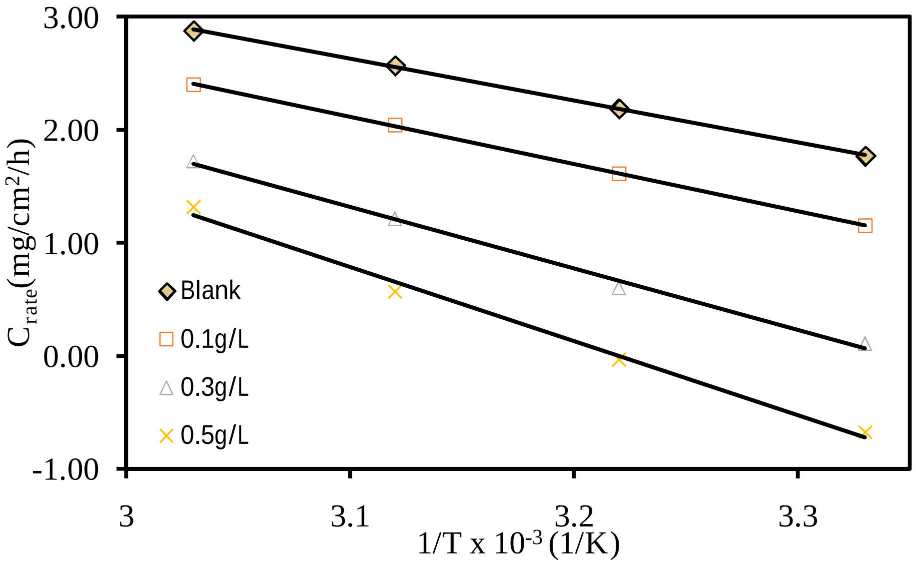


Figure 3.4.4: Arrhenius plot for the inhibition of corrosion of MS in1 N HCl without and with different concentrations of ECI extract.

Plots of Log $C_{rate}$/T versus 1/T for blank and for different concentrations of ECI extract gave straight lines as shown in Figure 3.4.5 with a slope ($-\Delta H_a/2.303R$) and an intercept of [(log(R/Nh) + ($\Delta S_a$ /2.303R)] on y-axis of these straight lines. These results are also given in Table 3.4.4. The values of $E_a$ and $\Delta H_a$ are close to each other as expected for the corrosion process in electrolytic solution.

Table 3.4.4: Thermodynamic activation parameters for MS in 1N HCl solution obtained from gravimetric measurements of ECI extract.

| Conc.(g/L) | $E_a$(kJ/mol) | $\Delta H_a$ (kJ/mol) | $-\Delta S_a$(J/mol/K) |
|---|---|---|---|
| Blank | 30.50 | 28.17 | 136.36 |
| 0.1 | 34.40 | 32.09 | 128.47 |
| 0.3 | 44.97 | 42.72 | 102.15 |
| 0.5 | 54.06 | 51.86 | 78.22 |

The positive value of $\Delta H_{a,}$ indicates that the corrosion process is endothermic in nature. The higher values of $\Delta H_a$ for inhibited solution are due to an increase in entropy of solvent (Zhang et al., 2014; Yadav et al., 2012).

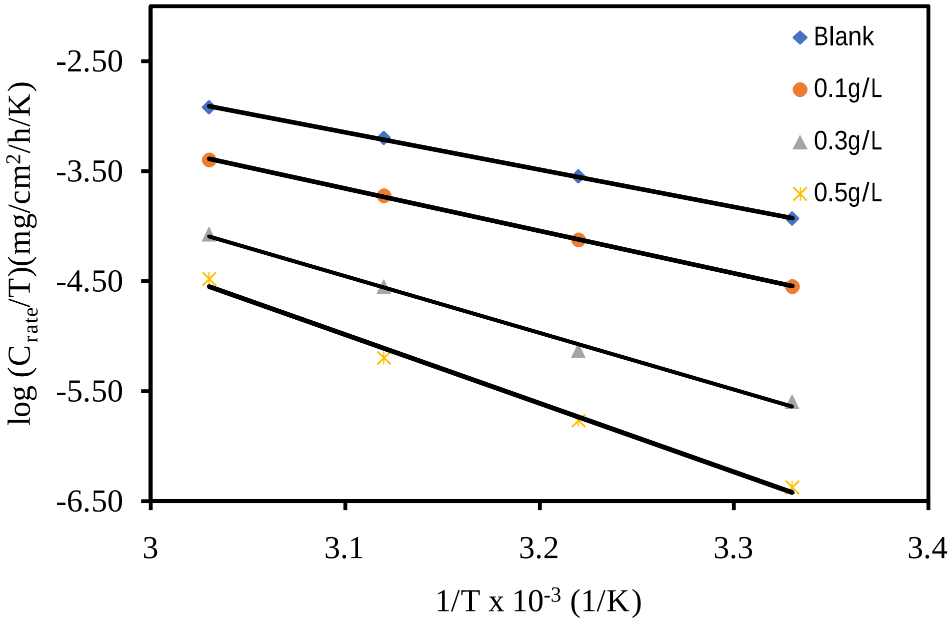


Figure 3.4.5: Transition state plot for MS corrosion in 1 N HCl at different concentrations of ECI extracts.

### 3.4.3. Electrochemical Measurements of ECI Extract

### 3.4.3.1. Measurement of Potentiodynamic Polarization of ECI Extract

The cathodic and anodic current potentials were measured for MS specimens in absence and presence of various concentrations of ECI extract (0.1 g/L-0.5 g/L) in 1 N HCl solutions at 300 K using Tafel polarization method which has been shown in Figure 3.4.6.

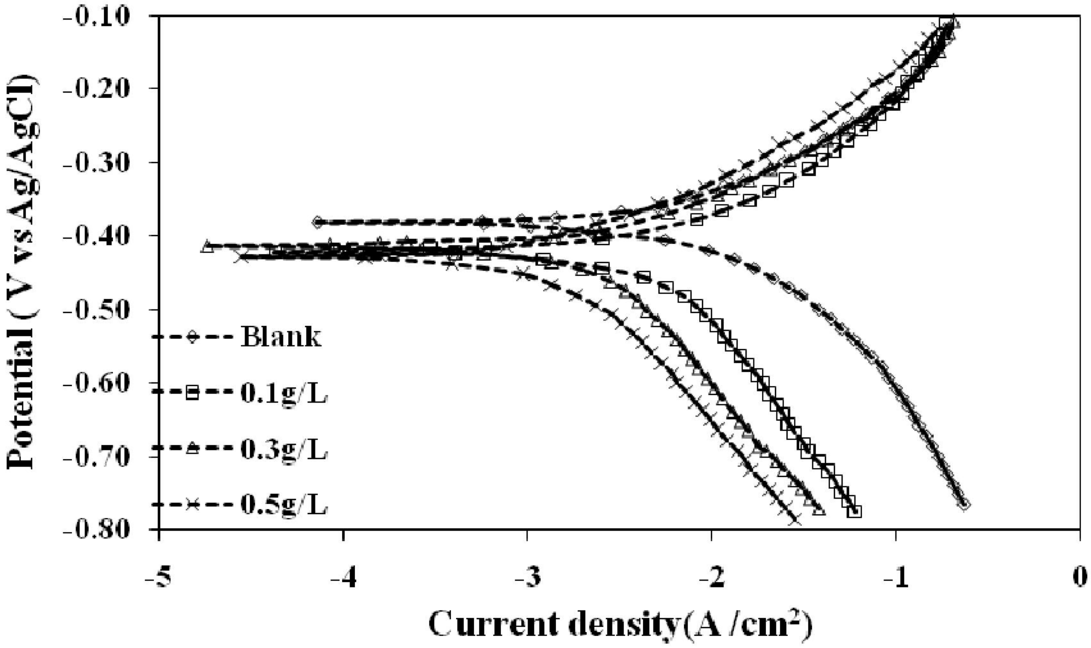


Figure 3.4.6: Tafel polarization curves for MS in 1 N HCl in absence and presence of various concentrations of ECI extract at 300 K.

The electrochemical parameters were calculated by extrapolation of the linear segments of the cathodic and anodic curves up to their interaction in Figure 3.4.6 and are listed in Table 3.4.5 along with $C_{rate}$ and %IE. It is evident from Figure 3.4.6 that at a given temperature the cathodic and anodic current densities decreases with increasing the concentration of ECI extract. The cathodic and anodic curves of the working electrodes in test solution (1 N HCl) shifted towards lower side with increasing the concentration of ECI extract which is a clear indication of inhibitive action of investigated plant extract. It is also observed that there is a decrease in $I_{corr}$ (Cf Table 3.4.5). The decrease in $I_{corr}$ is significant in cathodic region at all investigated concentrations of ECI extract. The displacement of $E_{corr}$ was around 66 mV towards the cathodic direction with respect to the blank, which shows a strong cathodic inhibitive property of ECI extract.

Table 3.4.5: Tafel polarization parameters obtained for MS in absence and presence of different concentrations of ECI extract in 1 N HCl at 300 K.

| Conc. (g/L) | $\beta_a$ (mV/dec) | $-\beta_c$ (mV/dec) | $-E_{corr}$V vs Ag/AgCl(mV) | $I_{corr}$ (µA/cm$^2$) | %IE |
|---|---|---|---|---|---|
| Blank | 162 | 243 | 362 | 10564 | 00 |
| 0.1 | 176 | 334 | 431 | 5978 | 43 |
| 0.3 | 143 | 326 | 431 | 2967 | 71 |
| 0.5 | 129 | 279 | 428 | 1014 | 90 |

Further, on the basis of the observed value of the displacement in $E_{corr}$ and previously reported data (Singh et al., 2016), it is concluded that Lengser inflorescence is a mixed type of inhibitor with dominant cathodic inhibitor (Gupta et al., 2016). Both $\beta_a$ and $\beta_c$ values of corrosive solution with ECI extract was changed significantly when compared with solution without ECI extract. This proves that ECI extract is a mixed type inhibitor. It is also seen that the cathodic curves of polarization are shooting up parallel with increasing the concentrations of inhibitor (Okafor et al., 2011). It means that the inhibitor does not change the mechanism of hydrogen evolution at a given temperature. This is attributed that the inhibitor molecules adsorbed onto the metal surface through a charge transfer mechanism. Thus, addition of these inhibitor molecules suppresses the cathodic processes and reduces the metal dissolution in acidic solution. It is also seen from Table 3.4.5, that the $\beta_c$ values is shifted toward more negative side of $E_{corr}$ values, whereas $\beta_a$ values slightly shifted toward lower $E_{corr}$ side. It is evident from the data tabulated in Table 3.4.5 that the %IE increases with increase in ECI concentrations, which indicates that the adsorption process favoured at higher inhibitor concentrations. The results suggest that on addition of ECI extracts the inhibitor molecules are adsorbed at metal/acid interface and decreases the intensity of corrosive attack by modifying the topography of metal surface.

#### 3.4.3.2. EIS of ECI Extract

Further, EIS has been conducted to confirm the adsorption of inhibitor molecules on to the MS surface. Figure 3.4.7 shows the Nyquist plots obtained by measuring the AC impedance for MS in 1 N HCl solution in the absence and presence of various concentrations of ECI extracts. The depressed semi-circular slope of Nyquist plots was observed in blank as well as in presence of different concentration of ECI extract.

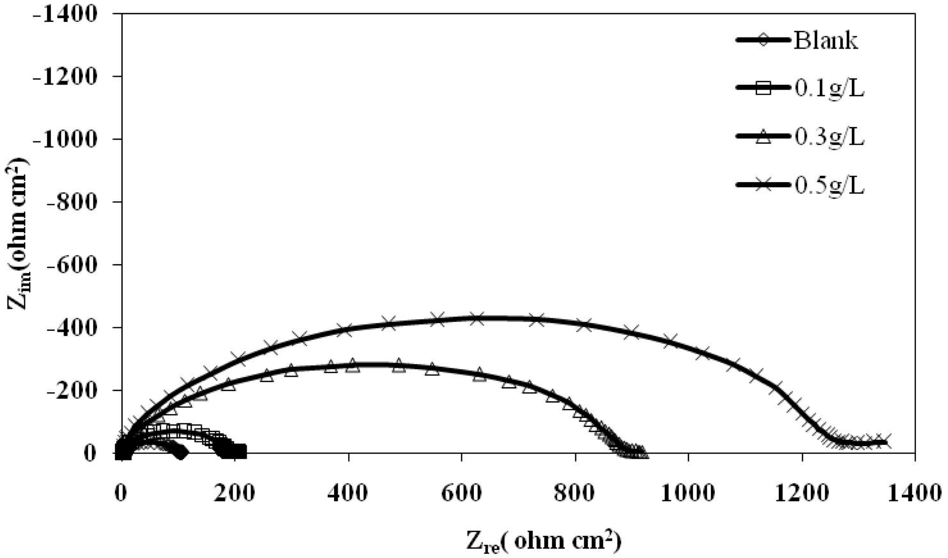


Figure 3.4.7: Nyquist plots for MS in 1 N HCl without and with different concentrations of ECI extract at 300 K.

The results indicate that inhibition mechanism could not depend on inhibitor concentration and corrosion control process is a charge transfer process (Awad and

Gawad, 2005; Karthik and Sundaravadivelu, 2016;Ali and Mahrous, 2017). Figure 3.4.8 illustrates that the diameters of impedance plots increases with increasing the concentration of ECI extracts, which points that extent of adsorption of inhibitor molecules on the MS surface increases with increasing the inhibitor concentrations. The charge transfer resistance ($R_{ct}$) refers to restriction of electron transfer from the anode to the cathode, which results in oxidation of the metal in the acidic solution. The resistive and capacitive behaviour that was observed at MS/test solution interface along with q and %IE were presented in Table 3.4.6.

Table 3.4.6: Impedance parameters for MS in 1 N HCl in absence and presence of different concentrations of ECI extract at 300 K.

| Conc. (g/L) | $R_s$ ($\Omega$ cm$^2$) | $R_{ct}$ ($\Omega$ cm$^2$) | $C_{dl}$ ($\mu$F/cm$^2$) | θ | %IE |
|---|---|---|---|---|---|
| Blank | 3.2 | 100.71 | 50.5 | 00.00 | 00.00 |
| 0.1 | 3.3 | 191.75 | 41.5 | 0.474 | 47.4 |
| 0.3 | 3.7 | 895.83 | 10.8 | 0.887 | 88.7 |
| 0.5 | 3.6 | 1278.3 | 0.99 | 0.921 | 92.1 |

The EIS data presented in Table 3.4.6 clearly indicates that the values of $C_{dl}$ decrease whereas the values of $R_{ct}$ increase with ECI concentrations. These results to observe a large diameter in Nyquist plot in presence of green inhibitor. The decrease in $C_{dl}$ values is interpreted as either formation of a prominent inhibitive film onto the metal surface i.e., increase in thickness of the electric double layer or decrease in dielectric constant of the solution or both (Qiang et al., 2016; Bai et al., 2015).

### 3.4.4. FT-IR of MS and ECI extract

The FT-IR spectra of the crude ECI extract as well the scratched protective film from MS surface immersed in 0.5g/L of ECI extract in 1 N HCl solution at 300 K are shown in Figure 3.4.8. The FT-IR spectra of the ECI extract and their corrosion reaction product on to the MS surface in inhibitive solution are recorded in the region of 400–4000 cm$^{-1}$. The results show a broad band appeared in the range of 3000–3600 cm$^{-1}$ which is assigned to the presence of -OH peak in ECI extract. This broad band in crude extract results from intermolecular hydrogen bonding (Kokalj, 2015; Wei et al., 2017).

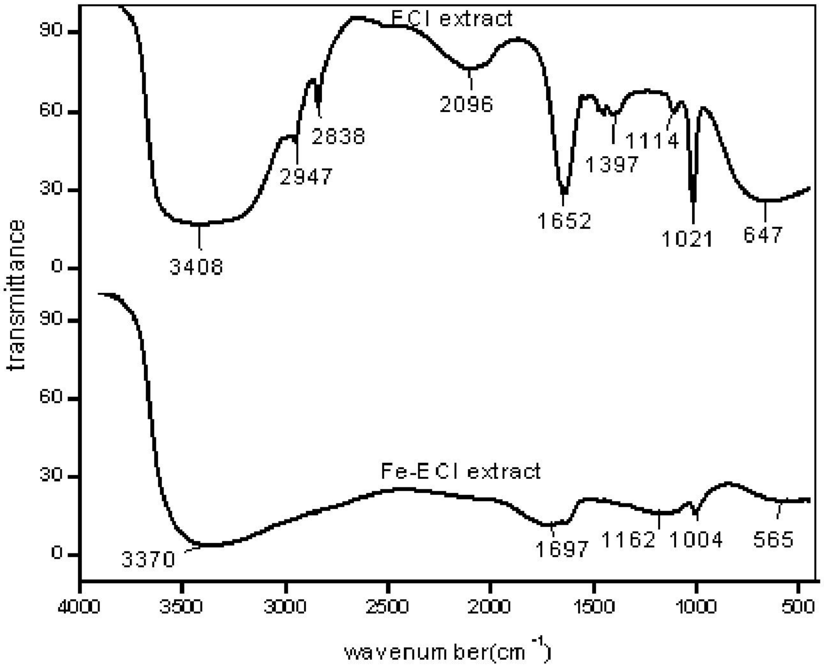


Figure 3.4.8: FT-IR spectra of (a) pure ECI extract and (b) protective layer developed on MS after immersion for 3 h in 1 N HCl containing 0.5g/L concentration of ECI extract.

This study following with GC-MS data presented in Table 3.4.1 suggests that the effective inhibitor molecules present in ECI extract are (-)-spathulenol, kryptogenin 2, 4-dinitro phenyl hydrazone, retinoic acid and its derivatives. The band appeared at 1114 $cm^{-1}$ in FTIR spectrum of crude extract is due to the -C-O-C stretching in retinoic acid and its derivatives. The strong peak near 1652 $cm^{-1}$ probably results from-COO- or C=C stretching in retinoic acid and its derivatives and band near 647 $cm^{-1}$is due to the -C=C-H stretching in crude ECI extract. The FT-IR spectrum of extract of corrosion product obtained by scratching from the MS surface showed a weak intensity band of –OH group at 3370 $cm^{-1}$. This is probably due to the formation of thin film of Fe-inhibitor complex onto the MS surface through –OH group due to presence of retinoic acid or spathulenol.

Disappearance of FT-IR bands near 1114 $cm^{-1}$and 647 $cm^{-1}$are due to physisorption of inhibitor molecules onto the MS surface. The change in intensity of different bands in the FT-IR spectra of corrosion products are due to change in the structure of inhibitor molecules in presence of metal which in turn felicitate the formation of Fe-inhibitor complex onto the MS surface in presence of ECI extract, which prevents the corrosion attack on metal surface. The shifting of spectral peaks in presence of 0.5 g/L of ECI extract is a clear indication of adsorption of phytochemicals from Lengser inflorescence extract on to MS surface.

### 3.4.5. SEM of MS Surface

The SEM images of the MS surface immersed in 1 N HCl for 3 hours in absence and presence of 0.5 g/L of ECI extracts along with MS surface before immersion were presented in Figure 3.4.9(a-c). A uniform surface of MS was observed without corrosive solution 3.4.9(b). Figure 3.4.9(a) and (c) present the SEM of MS surface topography in uninhibited and inhibited condition with 0.5g/L of ECI extract. Figure 3.4.9 (a) shows highly uneven surface of MS surface due to aggressive corrosion attack in presence of 1 N HCl solution. Figure 3.4.9(c) shows a remarkable decrease in the degree of corrosion due to presence of ECI extract as green inhibitor.

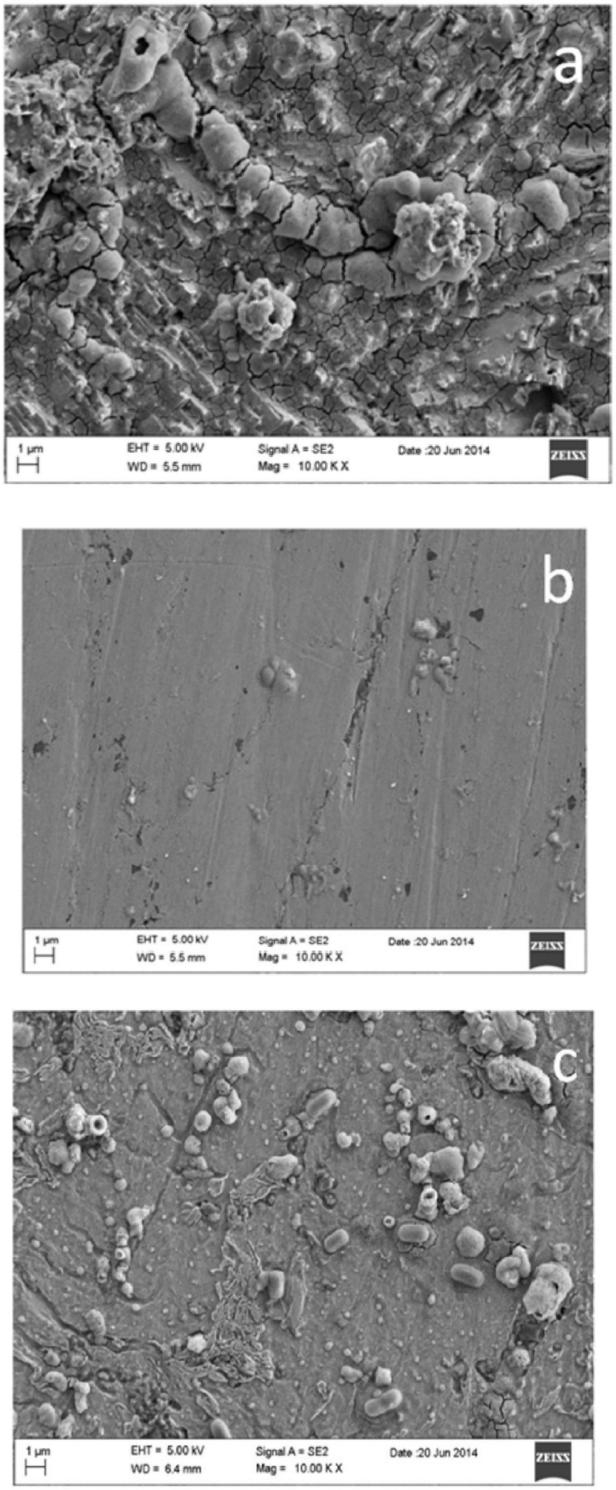


Figure 3.4.9: SEM images of MS surface topography: (b) before immersion in corrosive solution; (a) after immersion in 1 N HCl for 3 h; (c) after immersion in 1 N HCl solution containing 0.5 g/L ECI extract for 3 h.

### 3.4.6. Mechanism of Corrosion Inhibition of ECI Extract

Figure 3.4.10 shows a probable inhibition mechanism due to adsorption of phytochemicals from ECI extract on MS surface. The interaction between organic molecules present in ECI extract is attributed as follows:

i. Charge-transfer-type interaction between unshared electron pairs present in oxygen in carotenoids derivatives or pi-electrons of carotenoids and empty low energy d-orbitals of Fe atom present on MS surface.

ii. Columbic interactions between aromatic π- electron clouds and MS surface/solution interface or between protonated β carotenoids and adsorbed $Cl^-$ ions at cathodic sides.

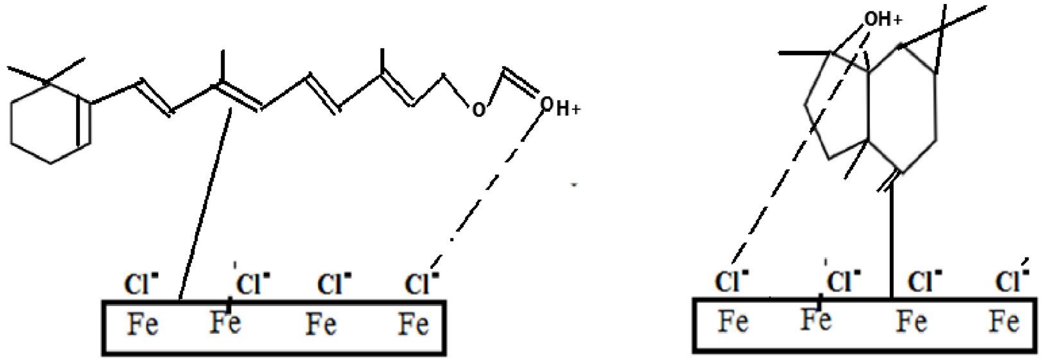


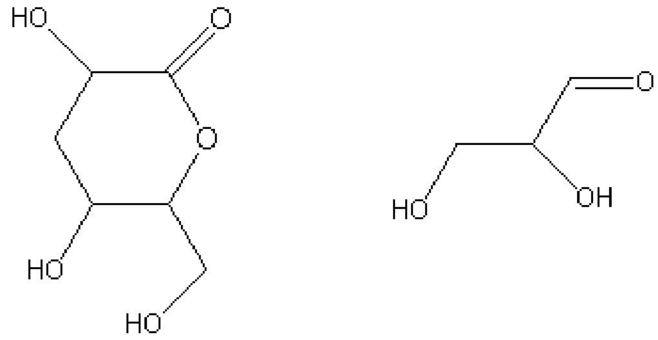
Figure 3.4.10: Schematic diagram of mechanism of corrosion inhibition reaction with main constituent of ECI extract on MS.

## 3.5. Extract of Melocanna baccifera Leaves (MBL)

### 3.5.1. Phytochemical Analysis of MBL Extract by GC-MS

The GC-MS analytical data obtained for the MBL extract are shown in Table 3.5.1 with their molecular weights. The results of GC-MS were obtained by measuring the peak area using Turbo Mass software and matched with the NIST library. Table 3.5.1 listed the various phytochemical constituents which contribute to the biological activity of MBL extract. The results revealed that the compounds such as 3-deoxy-d-mannoic lactone, 2, 3-dihydroxy propanal, 2-aminooxypentanoic acid, and guanosine were present as major compounds in the MBL extract.

In view of corrosion inhibition study, structures of few organic molecules are presented in Figure 3.5.1.



3-deoxy-d-mannoic lactone

propanal, 2,3-dihydroxy

Figure 3.5.1: Main phytochemical constituents in MBL extract.

Table 3.5.1: Chemical constituents present in the MBL extract using GC-MS analysis.

| Hit | Rev | For | Compound name | M.W | Formula | CAS |
|---|---|---|---|---|---|---|
| 1 | 924 | 702 | 3-deoxy-d-mannoic lactone | 162 | $C_6H_{10}O_5$ | 900127-87-1 |
| 2 | 876 | 669 | 3-deoxy-d-mannonic acid | 180 | $C_6H_{12}O_6$ | 900127-87-2 |
| 3 | 843 | 697 | 6-oxa-bicyclo [3.1.0] hexan-3-ol | 100 | $C_5H_8O_2$ | 25494-14-8 |
| 4 | 830 | 482 | endo-2,3-o-ethylidene-. beta. -d-erythrofuranose | 146 | $C_6H_{10}O_4$ | 77519-84-7 |
| 5 | 806 | 441 | (ss)- or (rr)-2,3-hexanediol | 118 | $C_6H_{14}O_2$ | 22520-19-0 |
| 6 | 801 | 696 | alpha. -d-glucopyranoside, methyl 3,6-anhydro- | 176 | $C_7H_{12}O_5$ | 13407-60-8 |
| 7 | 794 | 649 | 2-heptene, 1-ethoxy-, (z)- | 142 | $C_9H_{18}O$ | 51149-74-7 |
| 8 | 793 | 371 | pentanoic acid, 2-(aminooxy)- | 133 | $C_5H_{11}O_3N$ | 5699-55-8 |
| 9 | 791 | 526 | 2-formyl-9-[. beta. -d-ribofuranosyl] hypoxanthine | 296 | $C_{11}H_{12}O_6N_4$ | 125425-35-6 |
| 10 | 790 | 429 | 2-carbamyl-9- [. beta. -d-ribofuranosyl] hypoxanthine | 295 | $C_{11}H_{13}O_5N_5$ | 121358-21-2 |
| 11 | 783 | 492 | Propanal, 2,3-dihydroxy-, (s)- | 90 | $C_3H_6O_3$ | 497-09-6 |
| 12 | 782 | 429 | 2-hydroxymethyl-9- [. beta. -d-ribofuranosyl] hypoxanthine | 298 | $C_{11}H_{14}O_6N_4$ | 185377-94-0 |
| 13 | 781 | 597 | 2-t-butyl-4-methyl-5-oxo- [1,3] dioxolane-4-carboxylic acid | 202 | $C_9H_{14}O_5$ | 900191-45-5 |
| 14 | 778 | 533 | d-glycero-d-ido-heptose | 210 | $C_7H_{14}O_7$ | 900130-14-3 |
| 15 | 775 | 459 | rs-2,3-hexanediol | 118 | $C_6H_{14}O_2$ | 82360-67-6 |
| 16 | 767 | 495 | 1-deoxy-d-arabitol | 136 | $C_5H_{12}O_4$ | 900126-24-4 |
| 17 | 767 | 461 | l-gala-l-ido-octose | 240 | $C_8H_{16}O_8$ | 900130-12-1 |
| 18 | 763 | 629 | d-mannose | 180 | $C_6H_{12}O_6$ | 3458-28-4 |
| 19 | 762 | 522 | 2,3-epoxyhexanol | 116 | $C_6H_{12}O_2$ | 90528-63-5 |
| 20 | 761 | 514 | Guanosine | 283 | $C_{10}H_{13}O_5N_5$ | 118-00-3 |

### 3.5.2. Gravimetric Measurements of MBL Extract

Table 3.5.2 shows weight loss results for MS in 1 N HCl in the absence and presence of MBL extract at various concentrations. The data in Table 3.5.2 revealed that there is an increase in inhibition efficiency as the concentration of MBL extract increases and hence, corrosion rate is decreased (Hosseini et al., 2010). This behaviour is attributed to an increase in surface area covered by the adsorbed molecules on the MS surface as well as the increased MBL extract concentrations. Maximum inhibition efficiency of 93% is achieved at the MBL concentration of 0.5 g/L.

Table 3.5.2: Corrosion rate and surface coverage by weight loss in absence and presence of MBL extracts for 5 h.

| Conc. (g/ L) | $C_{rate}$ (mg/cm$^2$/h) | θ | %IE |
|---|---|---|---|
| Blank | 40.19 | 00.00 | 00.0 |
| 0.1 | 20.87 | 0.315 | 31.5 |
| 0.3 | 10.77 | 0.577 | 57.7 |
| 0.5 | 2.6 | 0.937 | 93.7 |

The Figure 3.5.2 reveals that the MBL extract inhibited the metal dissolution in chloride ion induced corrosion reaction of MS. The adsorption of main constituents compounds of MBL extract on the MS surface makes a protective layer between electrode-interface for mass and charge transfers.

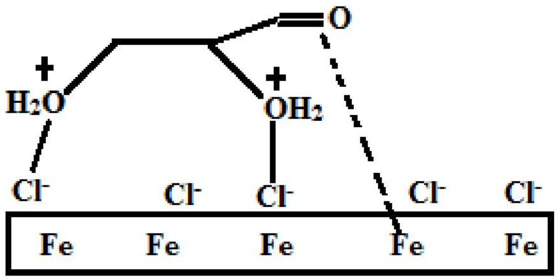


Figure 3.5.2: Schematic diagram of corrosion inhibition reaction mechanism of MBL extract on MS.

Therefore, the metal is protected from the $Cl^-$ of the HCl. The degree of protection increases with the degree of surface coverage by increasing concentration of inhibitor molecules on metal surface (Gadow et al., 2017). Inhibition of MS corrosion in 1 N HCl in the presence of the crude MBL extract is attributed to the adsorption of the phytochemical constituents such as 8-C-Glucosylapigenin, luteolin derivatives and chlorogenic acid of the MBL extract on the MS surface. It makes a protective layer on the metal surface from the corrosive $Cl^-$ present in solution thus reduces the corrosion reaction (Tanaka et al., 2014). The results of the preliminary phytochemical screening of different species of bamboo reveals that the crude extract contains alkaloids, tannins, general glycosides, saponnins, coumarins, alkaloids, flavonoids, anthraquinones and anthracene glycoside (Coffie et al., 2014). These substances contain polar functional groups along with hetero-atoms such as nitrogen, oxygen which have multiple bonds in their molecules with dense electron cloud which is easily coordinate with metal d-orbital of metal surface (Challouf et al., 2013; Murthy and Vijayaragavan, 2014; Fouda et al., 2015). The adsorption of inhibitor molecules on MS surface in aqueous acidic solution occur by replacing the adsorbed water molecules on metal surface. Chemical reaction involved in this process is as follows:

$$nH_2O\ (MS) + \text{Plant extract (solution)} \Leftrightarrow \text{Plant extract (MS)} + nH_2O\ (\text{solution})$$

It is seen from the table 3.5.2 that corrosion inhibition of MBL extract enhances with its increasing concentrations. This is due to the adsorption and the coverage of the inhibitor molecules on MS surface in acid medium.

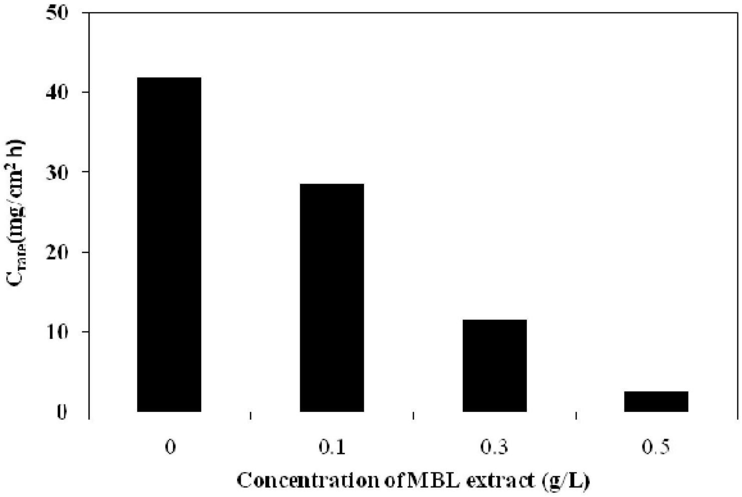


Figure 3.5.3: Corrosion rates of various concentrations of MBL extract on MS surface in 1 N HCl at 303 K.

### 3.5.3. Electrochemical Measurements of MBL Extract

#### 3.5.3.1. Measurement of Potentiodynamic Polarization of MBL Extract

Potentiodynamic polarization measurements provide the basic information of inhibitor on the anodic or cathodic inhibiting effect on electrochemical reaction of metal surface (Xu et al., 2015; Gopi and Kavitha, 2009). To ascertain these effects for MBL extract on MS, corrosion parameters are obtained on the basis of potential versus current density in the Tafel potential region. The electrochemical parameters $E_{corr}$, $I_{corr}$, %IE, anodic and cathodic Tafel slopes ($\beta_a$ and $\beta_c$) obtained from the polarization measurements are listed in Table 3.5.3 and polarization curves are shown in Figure 3.5.4.

It is observed that the addition of the inhibitors greatly affected both the anodic and cathodic processes as the curves are shifted towards lower corrosion current density region with respect to the blank (Cf. Figure 3.5.4). This is due to the fact that inhibitor molecules inhibiting both anodic and cathodic corrosion processes in electrolytic solution (Behpour et al., 2010; Li et al., 2007).

The shifts in corrosion current densities appear to be more dominant for the anodic curves than the cathodic curves. This suggests that the inhibitors, predominant, affected on the anodic reaction than the cathodic reaction. It could be observed from the data that $E_{corr}$ exhibited negative value with the addition of higher concentration of MBL extract. It is also seen that the presence of MBL extract molecules results in a marked shift in both cathodic and anodic branches of the polarization curves toward lower current densities. This means that the MBL extract affected both cathodic and anodic reactions. These results also suggest that inhibitors caused to reduce the anodic dissolution as well as to retard the hydrogen evolution reactions because of adsorption of MBL extract molecules on metal surface. This is primarily indicated the mixed-type of behaviour of anodic and cathodic current in the presence of the studied inhibitors. The inhibition efficiency of MBL extract by electrochemical method is also supported by weight loss method. The shift in $E_{corr}$ is due to blocking of active sites that occurred by the added inhibitor. In other words, the inhibitor decreases the surface area available for cathodic dissolution reaction.

Table 3.5.3: Corrosion parameters obtained from potentiodynamic polarization for MS in 1N HCl solution in the absence and presence of different concentrations of the MBL extract at 303 K.

| Conc. (g/ L) | $-E_{corr}$ ( mV vs Ag/AgCl) | $I_{corr}$ (mA/ $cm^2$) | -βc (mV/dec) | βa (mV/dec) | θ | %IE |
|---|---|---|---|---|---|---|
| Blank | 439 | 1.849 | 184 | 191 | 00.00 | 00.0 |
| 0.1 | 558 | 1.302 | 152 | 408 | 0.295 | 29.5 |
| 0.3 | 450 | 0.442 | 179 | 241 | 0.761 | 76.1 |
| 0.5 | 519 | 0.162 | 144 | 395 | 0.913 | 91.3 |

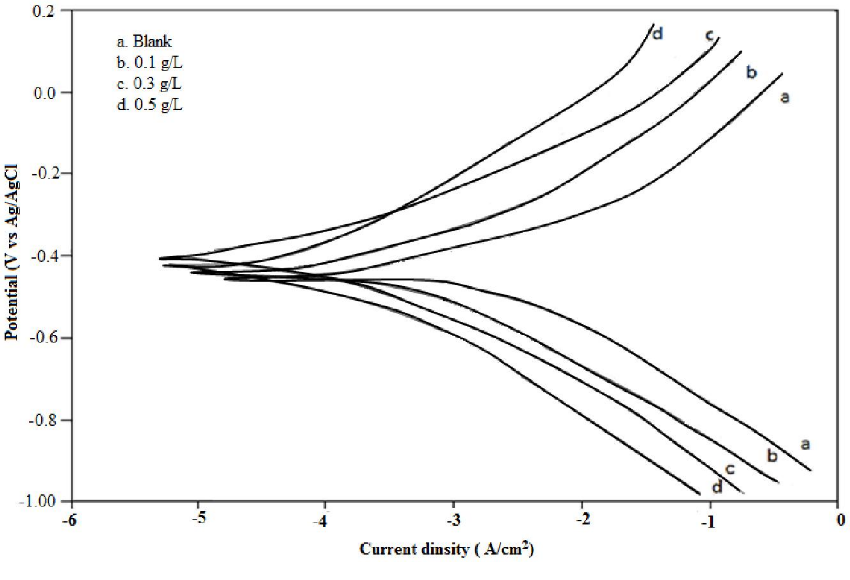


Figure 3.5.4: Tafel polarization curves of MS immersed in 1 N HCl with MBL concentration (a) Blank; (b) 0.1 g/L (c) 0.3 g/L (d) 0.5 g/L.

### 3.5.3.2. EIS of MBL Extract

The impedance responses of MS in 1 N HCl in the absence and presence of MBL extract is depicted in Figure 3.5.5. It is noticed from the Nyquist plots that the impedance is changed in the acid medium after the addition of MBL extract. The Nyquist plot is characterized by one semicircle capacitive loop corresponding to one time constant and suggesting that the corrosion of carbon steel is controlled by a charge transfer process. The resistive and capacitive behaviour that was observed at MS/test solution interface along with θ and %IE were presented in Table 3.5.4. The diameter of the semicircles in Nyquist plot was increased with an increase in concentration of MBL extract. This indicates the formation of an adsorption film over the steel surface. The observed decrease in the values of $C_{dl}$ which normally arises from a decrease in the dielectric constant and/or an increase in the double-layer thickness is a result of adsorption of MBL extract onto the metal/electrolyte interface (Umoren et al., 2014).

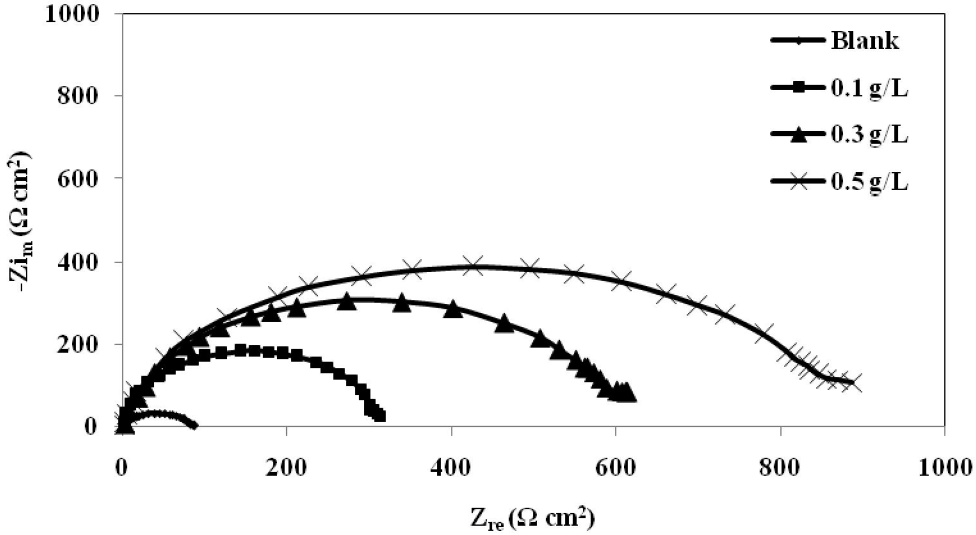


Figure 3.5.5: Nyquist plots for MS in 1N HCl without and with different concentrations of MBL extract at 303 K.

Table 3.5.4: Impedance parameters for MS in 1 N HCl solution in the absence and in the presence of different concentrations of MBL extract.

| Conc.(g/L) | $R_s$($\Omega$ cm$^2$) | $R_{ct}$($\Omega$ cm$^2$) | $C_{dl}$($\mu$F/ cm$^2$) | $\theta$ | %IE |
|---|---|---|---|---|---|
| Blank | 3.054 | 84.40 | 948 | 0.00 | 00 |
| 0.1 | 3.256 | 309.35 | 130 | 0.72 | 72 |
| 0.3 | 2.952 | 610.64 | 32 | 0.86 | 86 |
| 0.5 | 3.532 | 882.40 | 11 | 0.90 | 90 |

### 3.5.4. FT-IR of MS and MBL Extract

The band at 3200-3470 cm$^{-1}$ of the MBL spectrum in Figure 3.5.6 is due to stretching of the -O-H group. This band is shifted to 3300-3500 cm$^{-1}$ in the spectrum of the MBL-metal complex. The C=O stretching frequency shifts from 1600 cm$^{-1}$. It indicates about the participation of the heteroatoms of inhibitor adsorbed on metal surface.

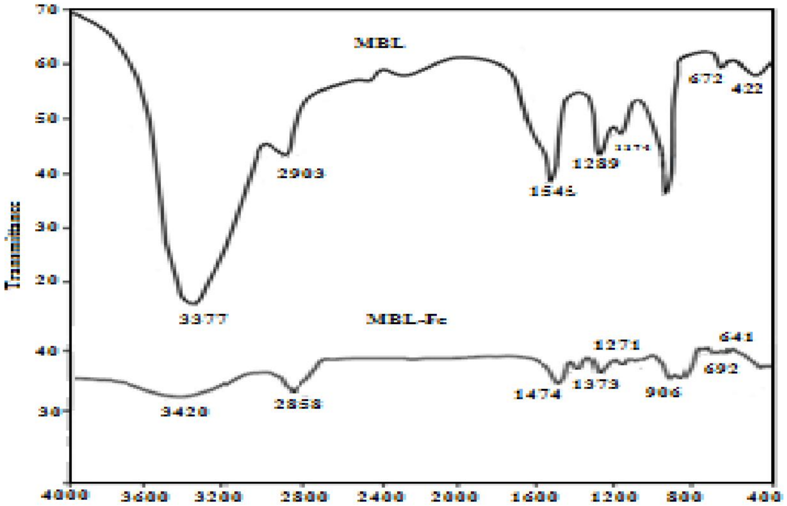


Figure 3.5.6: FT-IR spectrum of MBL extract and protective layer formed on metal surface (MBL-Fe) in 1 N HCl solutions.

### 3.5.5. SEM of MS surface

Microstructure studies of MS surface in corrosive medium (1 N HCl) was investigated in absence and presence MBL extracts at 303 K after 3-hour immersion by SEM and obtained results were shown in Figure 3.5.7 (a-b). Figure 3.5.7(a) shows rough and cracked surface of MS in the absence of inhibitor due to metal dissolution in corrosive medium. In the absence of inhibitor, a highly corrode surface is observed in Figure 3.5.7(a) due to more aggressive agent attack on metal surface in acidic solution (Kumari et al., 2017; Chaitra et al., 2017).

The topography of SEM image for MS surface with 0.5g/L of MBL extract shows in Figure 3.5.7(b). The SEM image obtained with inhibitor is significantly different from the blank solution without inhibitor in acidic solution. The rough surface formed on metal surface is decreased due to adsorptions of inhibitor molecules on metal surface and formation of protective layer, which prevents aggressive ions from contact between metal and corrosive medium. These observations are also in agreement with the result obtained from electrochemical measurements.

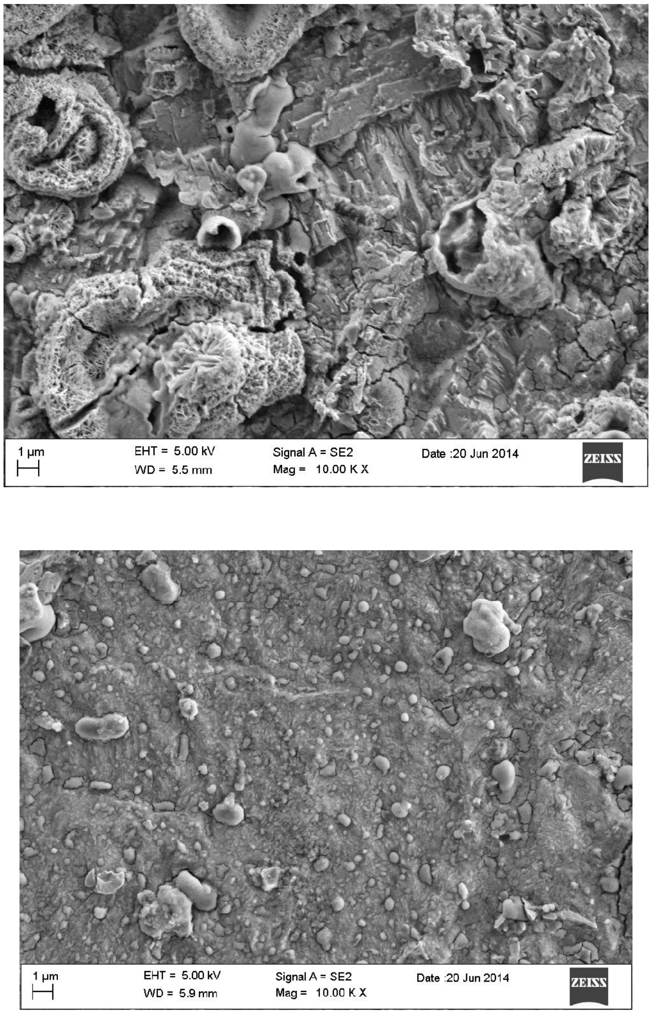


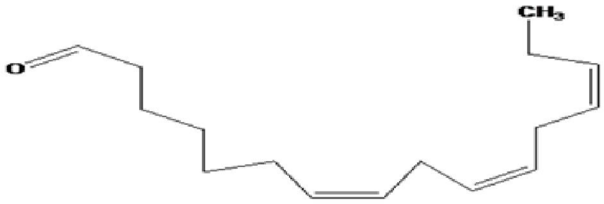
Figure 3.5.7: SEM image of MS specimen (a) after 3 h immersion in acidic solution and (b) after 3 h immersion in acidic solution with the 0.5g/L of MBL extract.

## 3.6. Extract of Spilanthes acmella (SA)

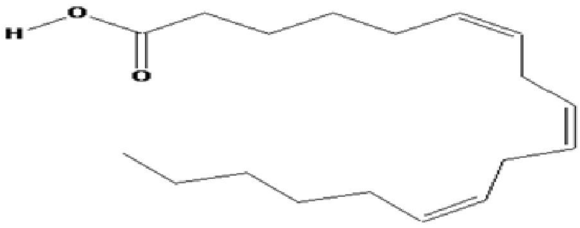
### 3.6.1. Phytochemical Analysis of SA Extract by GC-MS

The data obtained from the GC-MS analysis of the SA extract are shown in Table 3.6.1 with their molecular weights. The results of GC-MS are obtained by measuring the peak area using Turbo Mass software and matched with the NIST data library. In view of corrosion inhibition study, structures of few organic molecules are presented in Figure 3.6.1 whereas table 3.6.1 listed the various phytochemical constituents which contribute to the bioactive properties of SA extract. The results revealed that the compounds such as hexadecanoic acid, hepta-9, 10, 11-trienoic acid, octadecenoicacid, 5-hydroxylmethyl heptadecane, docosane aldehyde, methyl 11,14,17-eicosatrienoateand 1-thoxyoctadecane are present as some of major compounds in SA extract.

The bioactive constituents of the plant extract contained active compounds that might play to retardation of corrosion reaction in aggressive medium. This demonstrates an important role for SA extract as a new natural source of corrosion inhibitor.



cis,cis,cis-7,10,13-hexadecatrienal



gamolenic acid

11,14,17-eicosatrienoic acid, methyl ester

Figure 3.6.1: Structure of main constituent in crude SA extract.

Table 3.6.1: Chemical constituents present in SA extract using the GC-MS analysis.

| Hit | Rev | For | Compound name | M.W. | Formula | CAS |
|---|---|---|---|---|---|---|
| 1 | 963 | 902 | 9,12,15-octadecatrien-1-ol, (z,z,z)- | 264 | $C_{18}H_{32}O$ | 506-44-5 |
| 2 | 957 | 909 | 9,12,15-octadecatrienoic acid, (z,z,z)- | 278 | $C_{18}H_{30}O_2$ | 463-40-1 |
| 3 | 939 | 898 | 9,12,15-octadecatrienoic acid, methyl ester, (z,z,z)- | 292 | $C_{19}H_{32}O_2$ | 301-00-8 |
| 4 | 925 | 860 | cis, cis, cis-7,10,13-hexadecatrienal | 234 | $C_{16}H_{26}O$ | 56797-43-4 |
| 5 | 921 | 857 | 11,14,17-eicosatrienoic acid, methyl ester | 320 | $C_{21}H_{36}O_2$ | 55682-88-7 |
| 6 | 918 | 890 | 9,12,15-octadecatrienoic acid, (z,z,z)- | 278 | $C_{18}H_{30}O_2$ | 463-40-1 |
| 7 | 916 | 849 | 1,3,14,16-nonadecatetraene | 260 | $C_{19}H_{32}$ | 900131-11-2 |
| 8 | 906 | 828 | 8,11,14-eicosatrienoic acid, (z,z,z)- | 306 | $C_{20}H_{34}O_2$ | 1783-84-2 |
| 9 | 904 | 696 | methyl 8,11,14-heptadecatrienoate | 278 | $C_{18}H_{30}O_2$ | 900336-35-1 |
| 10 | 901 | 831 | Gamolenic acid | 278 | $C_{18}H_{30}O_2$ | 506-26-3 |
| 11 | 898 | 808 | 1,5,9,13-tetradecatetraene | 190 | $C_{14}H_{22}$ | 51487-38-8 |
| 12 | 892 | 847 | 1,6,9-tetradecatriene | 192 | $C_{14}H_{24}$ | 61233-71-4 |
| 13 | 883 | 638 | Methyl2-hydroxy-octadeca-9,12,15-trienoate | 308 | $C_{19}H_{32}O_3$ | 900336-39-1 |
| 14 | 883 | 789 | 7,10,13-hexadecatrienoic acid, methyl ester | 264 | $C_{17}H_{28}O_2$ | 56554-30-4 |
| 15 | 882 | 791 | 8,11,14-eicosatrienoic acid, (z,z,z)- | 306 | $C_{20}H_{34}O_2$ | 1783-84-2 |
| 16 | 881 | 800 | z-5,17-octadecadien-1-ol acetate | 308 | $C_{20}H_{36}O_2$ | 900131-06-9 |
| 17 | 880 | 646 | Methyl 11,14,17-eicosatrienoate | 320 | $C_{21}H_{36}O_2$ | 900336-41-3 |
| 18 | 879 | 733 | 9,12,15-octadecatrienoic acid, ethyl ester, (z,z,z)- | 306 | $C_{20}H_{34}O_2$ | 1191-41-9 |
| 19 | 878 | 739 | 9,12,15-octadecatrienoic acid, methyl ester, (z,z,z)- | 292 | $C_{19}H_{32}O_2$ | 301-00-8 |
| 20 | 877 | 819 | 9,12-tetradecadien-1-ol, acetate, (z,e)- | 252 | $C_{16}H_{28}O_2$ | 31654-77-0 |

### 3.6.2. Gravimetric Measurements of SA Extract

#### 3.6.2.1. Effect of SA Extract Concentration

Table 3.6.2 illustrate that there is a rapid decrease in corrosion rate with increasing concentration of SA extract. This is due to the fact that more inhibitor molecules are adsorbed on to the MS surface which protects from aggressive acidic medium. It is also noted that the surface coverage (θ) increases with increasing the inhibitor concentrations at working temperature of 300 K (Cf Table 3.6.2). Similar trends were observed by Li et al (2012) in their study of inhibition efficiency of bamboo leaves in acidic medium. The corrosion rate of MS in 1 N HCl was observed as 4.36 $mg/cm^2/h$ which are decreased to 0.41 $mg/cm^2/h$ in presence of 0.5 g/LSA extract with 90% surface coverage over MS. The effect of corrosion rate of MS in presence of varied concentrations of SA in acidic solution is shown in Figure 3.6.2. An ability to form metal inhibitor complexes with phytoconstituents of SA extract and their complexes with metal surface enables to reduce the metal dissolution in corrosive medium.

Thus, it is evident that the decrease in corrosion rate in the corrosive medium is due to the formation of protective film over the MS surface in presence of inhibitor molecules (Bin et al., 2014; Kosari et al., 2014). Corrosion Inhibitive property of the ethanol extracts of Musa sapientum peels was already reported by Eddy and Ebenso (2008). They found that the inhibitive action of plant extract is due to adsorption of inhibitor molecules on MS surface.

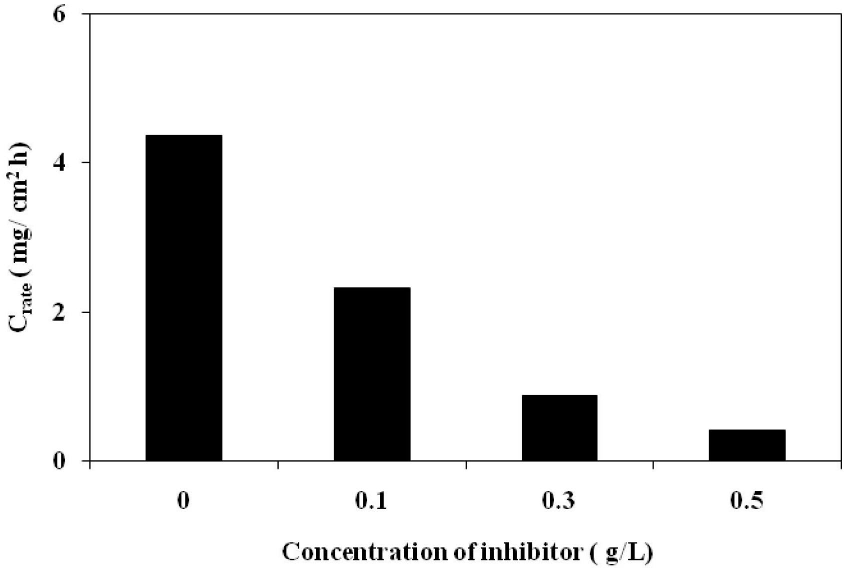


Figure 3.6.2: Corrosion rate of MS at various concentration of SA extract in 1 N HCl.

Table 3.6.2: Corrosion rate and inhibition efficiency at various concentration of SA extract in 1 N HCl at 300 K.

| Conc. (g/L) | $C_{rate}$ (mg/$cm^2$/h) | θ | %IE |
|---|---|---|---|
| Blank | 4.36 | 0.0 | 00 |
| 0.1 | 2.33 | 0.46 | 46 |
| 0.3 | 0.88 | 0.79 | 79 |
| 0.5 | 0.41 | 0.90 | 90 |

### 3.6.2.2. Effect of temperature

Figure 3.6.3 graphically represents the corrosion rate with an increase in temperature for MS in the presence of 0.5 g/L inhibitor. The molecules of SA extract are able to form metal inhibitor complex which lowers the interfacial interaction between metal and aggressive agent in acidic media enhancing the metal protection. The corrosion efficiency of SA extract decreased with increasing the temperature, which is due to the decomposition of phytoconstituents (Halambek et al., 2010) and desorption of the inhibitor molecules from metal surface.

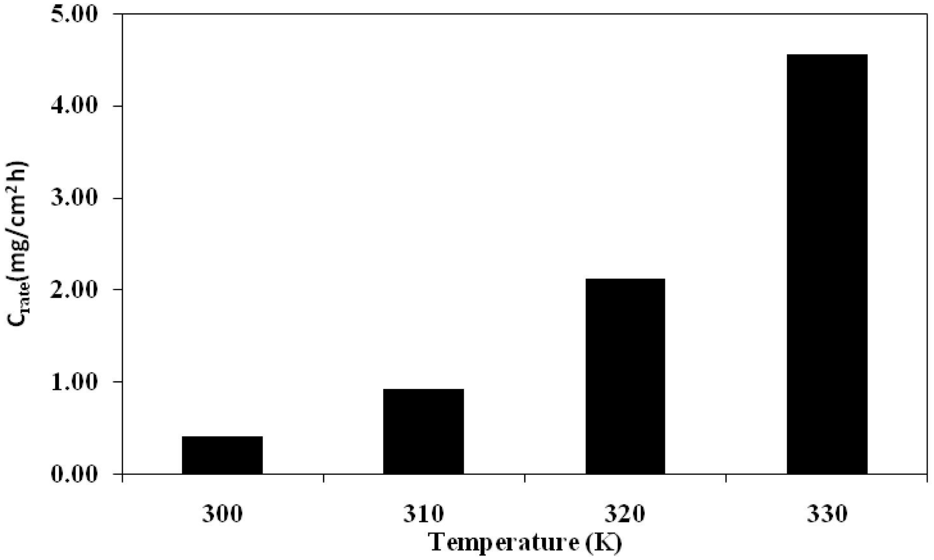


Figure 3.6.3: Variation of corrosion rate at different temperatures in presence of 0.5 g/L SA extract.

These properties are useful on metal protection, which is responsible for the corrosion inhibition of metals. However, increasing the temperature, adsorbed molecules on metal surface starts to leave the MS surface due to desorption process. This argument suggests that adsorption process was preferred at low temperature or at least to push the dissociation process due to phytochemical-metal weak bonds interaction on the MS surface. Figure 3.6.3 also reveals that dissociation is more at higher temperature hence increasing the corrosion rate.

### 3.6.2.3. Adsorption Isotherm of SA Extract

The correlation coefficient ($R^2$) and slope values for the studied isotherms are given in Table 3.6.3. It is observed that the correlation coefficient ($R^2$) for the Langmuir isotherm is least deviated from unity (Cf Figure 3.6.4). Hence, the Langmuir adsorption isotherm is best fitted in the present study. Langmuir adsorption isotherm assumes that the adsorbed molecules' forming a monolayer on the surface and no lateral interactions is occurred among the adsorbed inhibitor molecules (Aljourani et al., 2010).

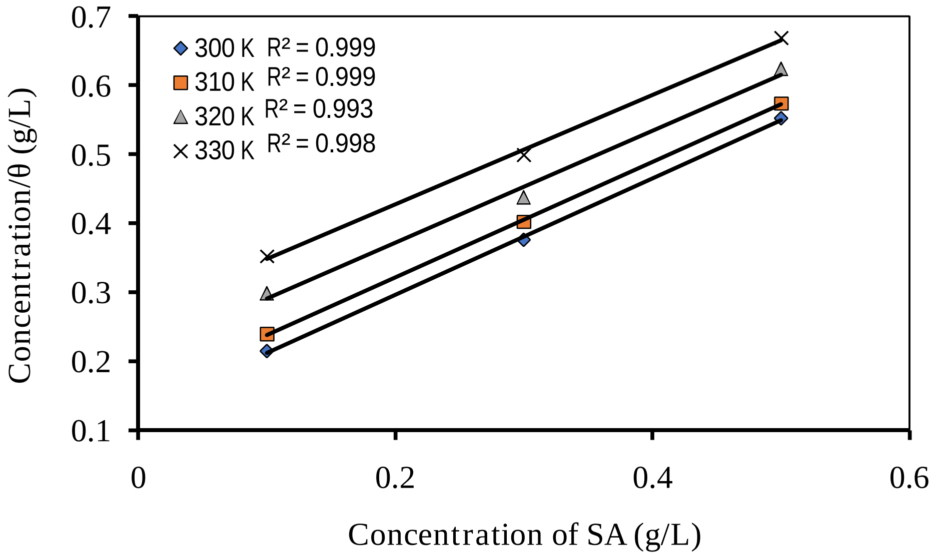


Figure 3.6.4: Langmuir adsorption isotherm at 300 K for MS in 1 N HCl with and without various concentrations of SA extract.

Using the intercept, $K_{ads}$ values are obtained and shown in Table 3.6.3. The free energy is found to be less than −20 kJ/mol. The negative value of standard free energy indicates a strong interaction and stability of the adsorption molecules on the metal surface (Jia et al., 2015). Generally, the magnitude of standard free energy around-20 kJ/mol is assumed to be electrostatic interaction causing physical adsorption.

The calculated thermodynamic parameters such as $E_a$, $\Delta H_a$ and $\Delta S_a$ are obtained and returned in Table 3.6.4.The value of $E_a$ in the absence of SA extract is lower than its presence i.e. 38.73 kJ/mol (blank) and 66.92 kJ/mol (0.5 g/L).Thus, the higher value of $E_a$ in the presence of SA extract reveals that adsorption of inhibitor molecules occurs over the MS surface increasing the energy barrier of the corrosion process.

Similarly, the values of $-\Delta S_a$ for SA extract are negative, indicating the activation stage of the adsorption process is controlled by associative interactions between the iron and the inhibitor molecules rather than the dissociative formation of iron and water molecules. The $\Delta H_a$ values are generally higher in presence of inhibitor compared to that of the uninhibited system which also indicates the effect of studied inhibitor on MS corrosion in the acidic medium.

Table 3.6.3: Calculated value of adsorption isotherms and respective free energy for the adsorption of SA extract on MS surface in 1 N HCl solution at different temperatures.

| Temp.(K) | Δ (kJ/mol) | ($K_{ads}$) |
|---|---|---|
| 300 | 15.14 | 7.81 |
| 310 | 14.67 | 6.47 |
| 320 | 13.91 | 4.77 |
| 330 | 13.28 | 3.71 |

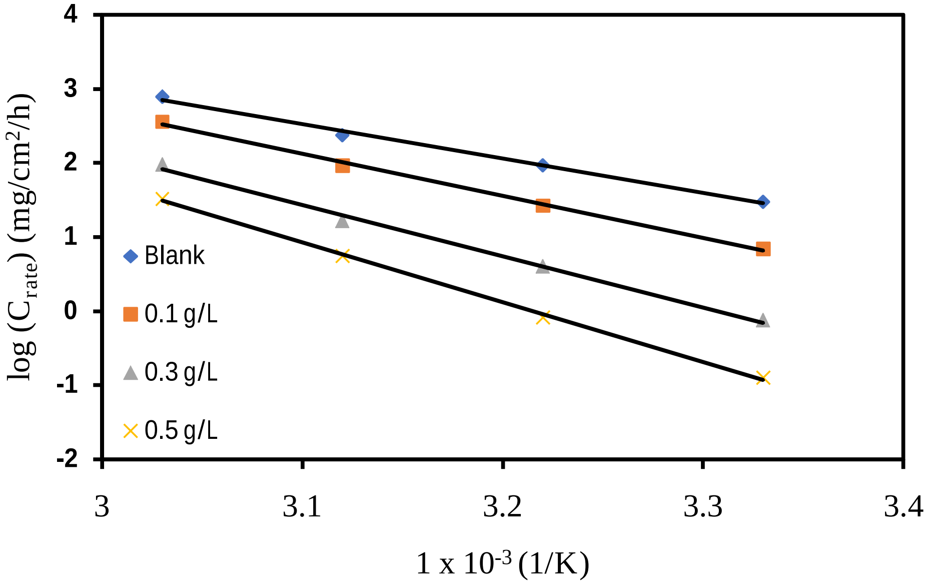


Figure 3.6.5: Arrhenius plots for the corrosion of MS in 1 N HCl solution in the absence and presence of the inhibitor in different concentration of SA.

Table 3.6.4: Arrhenius activation thermodynamic parameters for MS in 1 N HCl in the presence of various concentrations of SA extract.

| Conc.(g/L) | $E_a$(kJ/mol) | $\Delta H_a$(kJ/mol) | $-\Delta S_a$(J/mol/K) |
|---|---|---|---|
| Blank | 38.73 | 36.09 | 112.64 |
| 0.1 | 47.12 | 44.49 | 89.96 |
| 0.3 | 57.43 | 54.80 | 63.74 |
| 0.5 | 66.92 | 64.28 | 38.55 |

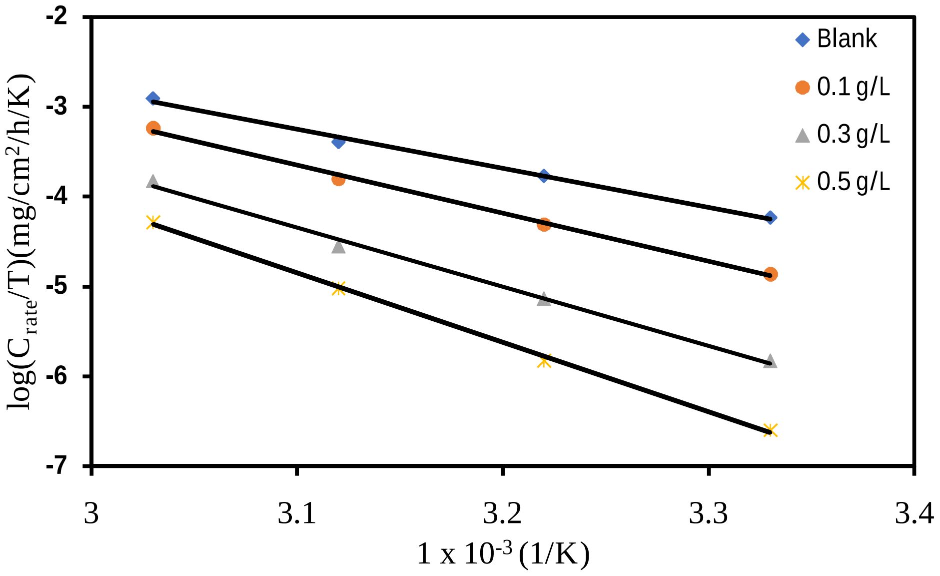


Figure 3.6.6: Transition plots for the corrosion of MS in 1 N HCl solution in the absence and presence of the SA extract.

### 3.6.3. Electrochemical Measurements

#### 3.6.3.1. Measurement of Potentiodynamic Polarization of SA Extract

Further to understand the corrosion inhibition of SA extract for MS in acidic medium, the Tafel polarization techniques are used at 300 K (Chakravarthy et al., 2014; Fouda et al., 2017; Geethamani and Kasthuri, 2015). The Tafel polarisation curves for MS in the HCl solution in the absence and presence of SA extract are given in Figure 3.6.7.

The polarisation curve is shifted to more negative and more positive potentials with respect to the blank polarisation curve, with increasing the concentration of SA extracts. These observations indicate that the SA extract is a mixed-type inhibitor for the corrosion of MS in 1 N HCl at 300 K (Gadow and Motawea, 2017). It is also found that the cathodic polarization curves slightly shifted towards negative region whereas anodic polarization curve shifted with greater extent, which means the inhibition of corrosion reaction is predominant with anodic dissolution reaction in acidic medium (Zhao and Chen, 2012).

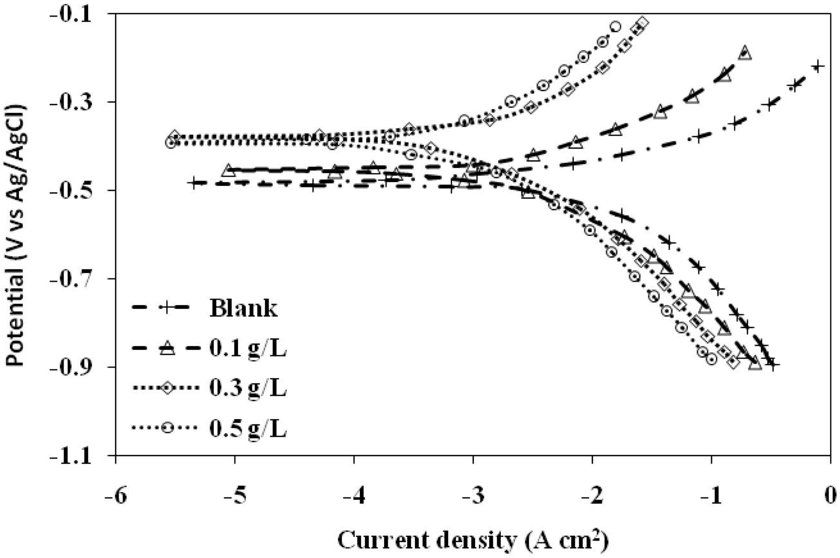


Figure 3.6.7: Potentiodynamic polarization curves for MS in 1 N HCl solution without and with different concentrations of SA extract at 300 K.

The cathodic and anodic potentiodynamic polarization parameters are obtained by Tafel extrapolation techniques and the resulting potentiodynamic polarization parameter viz., $E_{corr}$, $I_{corr}$, $\beta_c$ and $\beta_a$, are shown in Table 3.6.5 (Gadow and Motawea, 2017). The polarization curves of MS in acidic solution without inhibitor possesses the value of $\beta_a$ 191 mV/decade, $\beta_c$ is -184 mV/ decade and $E_{corr}$ 482 mV.

The corrosion potential ($E_{corr}$) is shifted by 425 mV, 316 mV and 337 mV in the positive direction after addition of 0.1 g/L, 0.3 g/L and 0.5 g/L of SA extract in acidic solution, respectively. Hence, the SA extract is recognized as a strong inhibitor of anodic process. Other electrochemical parameters and the inhibition efficiencies of different concentrations of plant extracts are determined from $I_{corr}$ with and without plant extract and shown in Table 3.6.5. Further, Table 3.6.5 shows the inhibition efficiency of the plant extract which is increased by 67.72%, 86.63% and 91.47% by the addition of 0.1g/L, 0.3g/L and 0.5g/L of inhibitor in acidic solution, respectively. This result is in good agreement with the gravimetric studies; however, the %IE value obtained from polarization method is different from weight loss method and this difference is due to the different analytical techniques used in the data analysis (Hegazy et al., 2010)

Table 3.6.5: Measurement of electrochemical parameters for the MS in 1 N HCl solution in absence and presence of different concentration of SA extract at 300 K.

| Conc. (g/L) | $\beta_a$ (mV/dec) | -$\beta_c$(mV/dec) | -$E_{corr}$ (mV vs Ag/AgCl) | $I_{corr}$($\mu A/cm^2$) | %IE |
|---|---|---|---|---|---|
| Blank | 114 | 306 | 482 | 16880 | 00.0 |
| 0.1 | 131 | 284 | 425 | 5448 | 67.7 |
| 0.3 | 193 | 296 | 316 | 2255 | 86.6 |
| 0.5 | 182 | 299 | 337 | 1440 | 91.4 |

### 3.6.3.2. EIS of SA Extract

EIS is a powerful and non-destructive tool for studying the electrochemical corrosion processes of MS in corrosive environments and determining the inhibition ability of various corrosion inhibitors (Pan et al., 2009). Figure 3.6.8 shows Nyquist plots of the MS electrode with and without SA extract while table 3.6.6 shows the estimated values of the $R_s$, $R_{ct}$, and $C_{dl}$ at the metal/inhibitor interface, respectively. It is seen that the presence of SA extract caused to enhance the values of $R_{ct}$. The increase in

$R_{ct}$ value is due to the adsorption of SA extract and forming a protective layer on the metal surface. An intact protective film can act as a barrier for water, oxygen and corrosive anions on the metal surface. The enhances $R_{ct}$ values due to the gradual replacement of water molecules by inhibitor molecules present in high concentration on the metal surface and thus decreasing the extent of MS dissolution in corrosive medium. Hence, SA extract has good protection for MS in corrosive medium.

As shown in Fig. 3.6.8, all Nyquist plots exhibit one single capacitive loop, indicating that the corrosion of MS in 1 N HCl with and without protection is mostly controlled by charge transfer processes and double layer capacitance. In addition, these impedance spectra show a similar shape at all tested concentrations of inhibitor, which suggests that corrosion mechanism is not changed significantly. As compared to the diameter of blank solution, the diameter of the semicircles is increased with the addition of SA extract. This indicates the inhibitive capability of SA extract. Besides, these Nyquist plots are having depressed semicircles under the real axis, which is known as frequency dispersion effect and it is due to the surface roughness, heterogeneity and grain boundaries available on the metal surface (Juttner, 1990).

As evident from Table 3.6.6, the $C_{dl}$ value is decreased with the increase in concentration of inhibitor. This is due to the decrease in the extent of corrosion in corrosive medium. The low $C_{dl}$ values are associated with slower corroding processes and this is an indication of decrease in the local dielectric constant and or an increase in the thickness of the electrical double layer (Noor, 2014; Kadhum et al., 2014). This proves the adsorption of the corrosion inhibitor molecules at metal/solution interface. It is clear from the table that the addition of the inhibitor caused a significant change in the impedance response of the MS specimens immersed in the inhibitor-free solution.

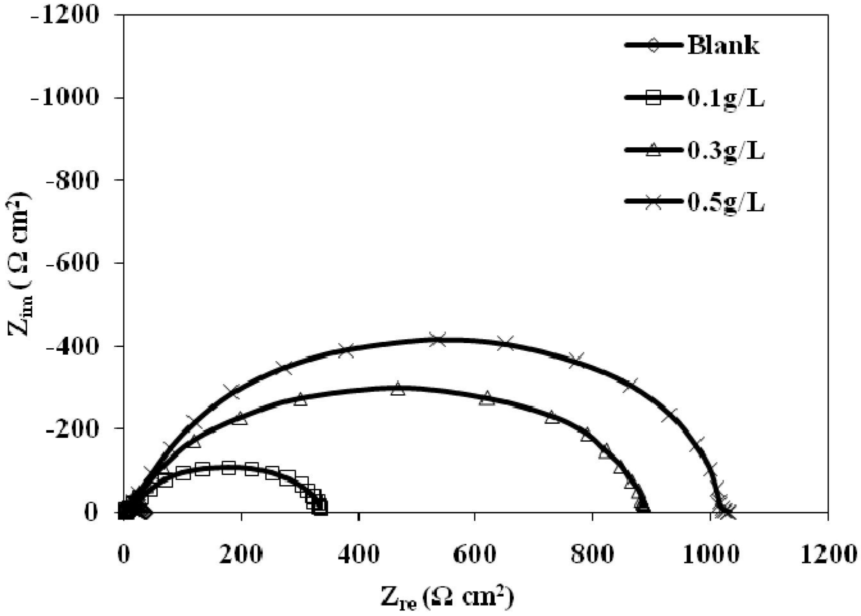


Figure 3.6.8: Nyquist plots for MS in 1 N HCl solution without and with different concentrations of SA extract at 300 K.

Table 3.6.6: Impedance parameters for MS in 1 N HCl solution in the absence and in the presence of different concentrations of SA extract.

| Conc. (g/L) | $R_s$(Ω cm$^2$) | $R_{ct}$(Ω cm$^2$) | $C_{dl}$(μF/cm$^2$) | θ | %IE |
|---|---|---|---|---|---|
| Blank | 2.05 | 118 | 213 | 00.00 | 00.00 |
| 0.1 | 2.34 | 351 | 29 | 0.663 | 66.3 |
| 0.3 | 2.61 | 905 | 45 | 0.869 | 86.9 |
| 0.5 | 3.02 | 1046 | 39 | 0.887 | 88.7 |

### 3.6.4. FT-IR of MS and SA Extract

The FT-IR spectra of the SA extract and the protective layer of the extract molecules adsorbed onto the MS surface are shown in Figure 3.6.9. In the Figure 3.6.9, a broad band at 3389 $cm^{-1}$ represented the O-H stretching vibrations. A weak band appeared at 2951$cm^{-1}$is due to the C-H stretching vibrations. The bands at 1653 $cm^{-1}$ and 1021 $cm^{-1}$ corresponded to the C=C and C-O-C stretching vibrations. The spectral peaks of scratched corrosion product in the presence of 0.5 g/L SA extract are shifted to 3401 $cm^{-1}$ and 1663 $cm^{-1}$ respectively for the characteristics of C=C, C=O or O-H functional groups of plant extract involved in bonding with iron atom. Thus, it is concluded that the plant extract molecules are adsorbed onto the metal surface at the active sites.

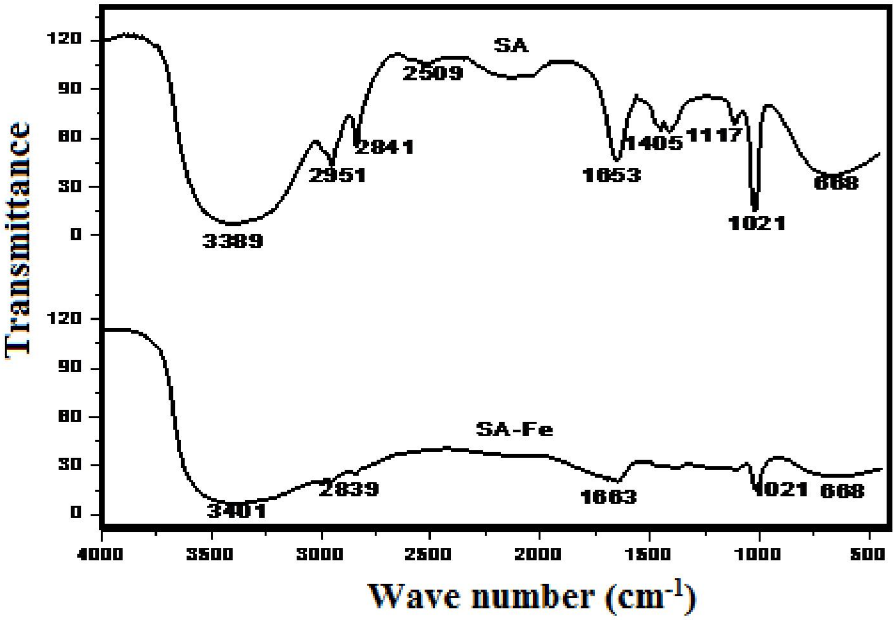


Figure 3.6.9: FT-IR spectra of (SA-Fe) scratched surface of MS containing 0.5 g/L of SA extract after 3 h.

### 3.6.5. SEM of MS surface

Microstructure study of MS surface in corrosive medium (1 N HCl) is investigated in absence and presence of SA extracts at 300 K after 3-hour immersion using the SEM images and obtained results are shown in Figure 3.6.10(a-c). The clean surface before immersion in test solution is shown in Figure 3.6.10 (a); it shows a non-cracked surface. Figure 3.6.10(b) exhibits the effect of 1 N HCl solution without inhibitor on the corrosion of steel sample at 300 K. In the absence of inhibitor, a highly corroded surface is observed in Figure 3.6.10(b) due to more aggressive corrosive attack on metal surface in acidic solution (Kumari et al., 2017; Chaitra et al., 2017). Figure 3.6.10(b), observed rough surface due to higher chloride concentration on metal surface and it enhanced the metal dissolution in acidic solution.

The topography of the MS surface with 0.5g/L of SA extract in acidic solution after 3h shows in Figure 3.6.10(c). The SEM image obtained with inhibitor is significantly different from the blank solution without inhibitor in acidic solution. The rough surface formed on metal surface is decreased due to adsorption of inhibitor molecules on metal surface and formation of protective layer, which prevents contact of aggressive ions towards the metal surface. These observations are also in agreement with the result obtained from electrochemical measurements.

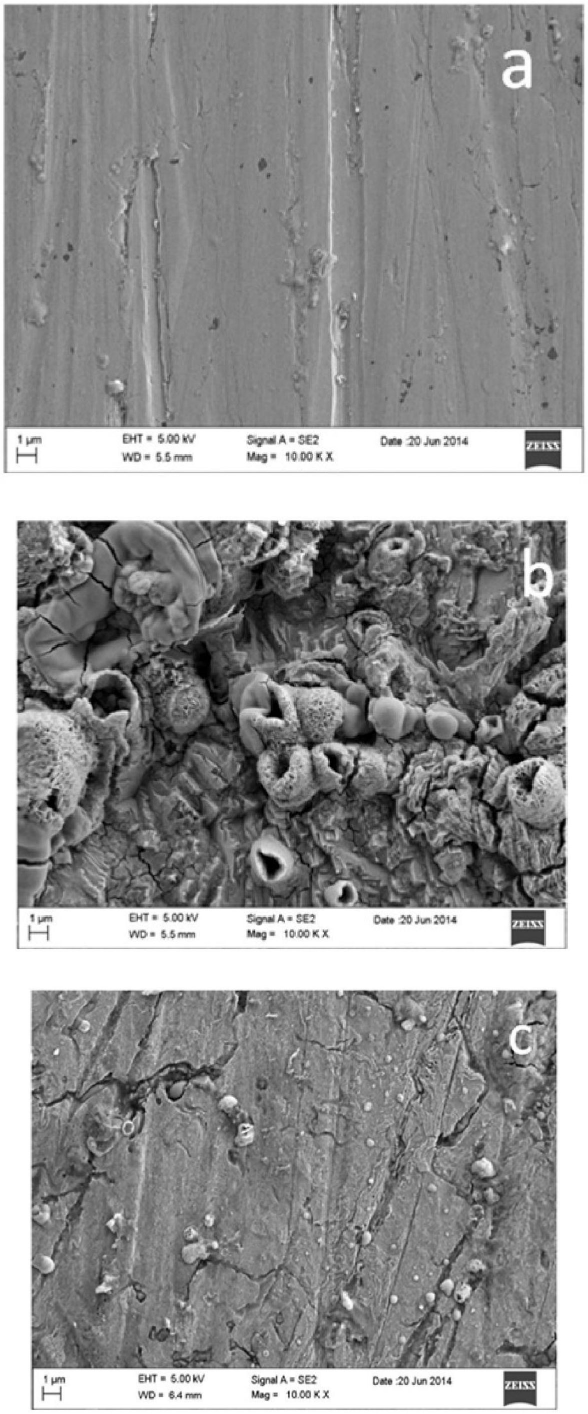


Figure 3.6.10: SEM image of MS specimen (a) before immersion in acidic solution (b) after 3 h immersion in acidic solution and (c) after 3 h immersion in acidic solution with the 0.5 g/L of SA extract.

### 3.6.6. Mechanism of Corrosion Inhibition of SA Extract

The results of the present study showed that the corrosion inhibition of MS was due to adsorption of phyto-chemicals on the MS surface. The protonated forms of oxygen present in phytochemicals get adsorbed onto the negatively charged MS surface (chloride ions) through electrostatic interaction (Lgaz et al., 2018). The π-electrons present in phytochemicals are interacted with the MS surface by donor-acceptor between π-electrons and vacant d-orbital of the metal surface (d-orbitals of surface Fe-atoms).

Inspection of the structure in Figure 3.6.11 reveals that $Cl^-$ is adsorbed on metal surface and interacts with inhibitor cations to form protective layer on the MS surface. This layer prevents the surface from aggressive anions (Yousefi et al., 2015). The presence of π bonds may also lead to the formation of protective layer on metal surface (Gupta et al., 2016). This adsorption gives rise to a large covered surface area with a small number of adsorbed molecules. Therefore, high inhibition efficiency is obtained by relatively low concentrations of the SA extract.

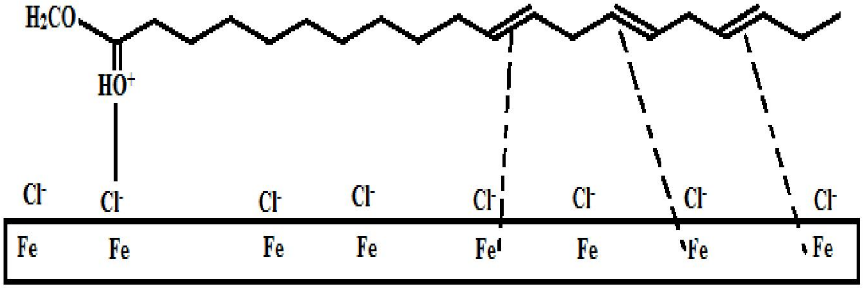


Figure 3.6.11: Schematic diagram of the adsorption process of SA extract MS surface in 1 N HCl.

## 4. Summary and Conclusions

The relevant observations and the important findings of the present investigation on corrosion inhibition of MS in acidic medium using various plant extracts are summarized and the main conclusions drawn from the study are discussed in this chapter.

Cleaning and mild steel (MS) related machinery is necessary for contaminate free production of product. The equipment gave best performance when, clean and maximum resistance to corrosion. However, cleaning agents are corroding the equipment hence, increases the operational and maintenance costs (Romero et al., 2010). During cleaning processes transportation of MS and processing of some chemical industry corrosion inhibitors are used to minimize the corrosion to maximize the production of good quality product (Rahse, 2014).

### 4.1. Corrosion Inhibition Studies using Allium hookeri (AH) Extract

This is worth to mention here that the present study involved a detailed phytochemical investigation in AH extract using GC-MS, which helps to identify the major inhibitive components present in it. The identified compounds are glucose derivative, 2-penten-1-ol, and isosorbide with O-atoms and π-bonds in crude AH extract. The inhibitive action of the extract is mainly due to the carbohydrate derivatives. The weight loss measurements indicated that the corrosion rate of MS in 1 N HCl was observed as 4.71 mg/cm$^2$/h which was decreased to 0.32 mg/cm$^2$ h in present of 0.5 g/L AH extract with 93% surface coverage over MS surface.

Langmuir adsorption isotherm studies show that the value of $K_{ads}$ decreases with an increase in temperature. This indicates that the strength of adsorption bond on metal surface is decreased and hence show lower inhibition efficiency at higher temperatures. The obtained value of standard free energy in temperatures (300 K- 330 K) are less negative standard free energy around (– 20 kJ/mol) are usually characteristic of physical adsorption of inhibitor molecule on to the metal surface.

Arrhenius-type dependence on thermodynamic parameters for corrosion inhibition process shows that increasing the activation energy value, when compared to the blank solution, is generally interpreted as an indication of the formation of an adsorptive film. The positive signs of $\Delta H_a$ reflects the dissolution of MS is slower in the presence of inhibitor. The entropy of activation $\Delta S_a$ in the absence of inhibitor is large due to more extent of metal dissociation.

Potentiodynamic polarization measurements show that AH extract suppressed both the anodic and cathodic reactions. It is observed that the anodic branches shifted towards lower corrosion current density with increasing concentration of inhibitor and hence higher value of $ß_a$ over $ß_c$. It means that the cathodic reaction is predominant. It is observed from the data that the addition of AH extract caused to decrease the corrosion current density ($I_{corr}$) which is due to the adsorption of the inhibitor on the metal surface. The change of $R_{ct}$ and $C_{dl}$ values are attributed to the adsorption of inhibitor on the metal surface which decreases the extent of metal dissolution in corrosive medium (Karthik et al., 2015; Kumar et al., 2017). Further, the value of $R_{ct}$ is increased as the diameter of Nyquist loop increases with increasing concentration of AH extract, however the $C_{dl}$values decreases simultaneously.

In the FTIR spectra of scratched surface of corrosion product with 0.5 g/L, it is seen that changing the intensity of band of some important functional group such as asymmetric -$CH_3$ stretching band at 2957 cm-$^{1}$ and thiol (-SH) stretching band at 1401 cm$^{-1}$ are completely disappeared, while the some band shifted such as –OH (3396 cm$^{-1}$), –C=O (1639 cm$^{-1}$) and C–C ring bending (606 cm$^{–1}$) is due to adsorption of these functional group on to metal surface. This information provides us as corrosion inhibitive functional group contained with heteroatom and multiple bonds which are present in AH extract blocking the active sites of MS surface.

## 4.2. Corrosion Inhibition Studies using Clerodendrum colebrookianum (CCWL) Extract

The analysis of GC-MS data of methanolic extract of CCWL revealed the presence of major components as cyclohexanol derivative, 3, 7, 11, 15-tetramethyl-2-hexadecen-1-ol, butanoic acid, 3, 7-dimethyl-6-octenyl ester and phytol. The weight loss measurement reveals the corrosion rate of MS in 1 N HCl. It was observed that the weight loss of MS was decreased from 3.25 mg/cm$^{2}$/h to 0.15 mg/cm$^{2}$ h in presence of 0.4 g/L of CCWL extract with 95% surface coverage over MS. The corresponding value of standard free energy is found to be in between the -26.69 to -28.45 kJ/mol, which suggests that the adsorption of CCWL extract over the MS surface is physisorption along with the electrostatic interactions occurred between the inhibitor and the charged metal surface.

It is also noticed from the weight loss data that the corrosion rate for MS in1 N HClis increased with an increase in temperature from 303 K to 333 K. The inhibitor molecules diffuse back into the solution from MS surface with increase in temperature hence, more surface area of MS is exposed to the acid medium.

It is observed from the polarization curves that $I_{corr}$ decreases with increasing the concentration of CCWL extract in acidic media. This indicates that inhibitor suppresses the dissolution of iron whereas the variation of cathodic Tafel slope suggests that the presence of CCWL extract suppresses significantly the hydrogen evaluation reaction.

Further, the Nyquist plots possesses single semicircle capacitance loop which indicates charge transfer corrosion process. The diameter of capacitive loop increases with an increase in concentration of inhibitor. This suggests the decrease of corrosion rate due to adsorption of inhibitor species or species like $H^+$ on the electrode surface. It is also found that a significant decrease in $C_{dl}$ on addition of inhibitor but value increases with increasing the inhibitor concentration. This result leads to decrease in the local dielectric constant or an increase in the thickness of the electrical double layer and suggests that the inhibitor molecules form a protective layer at the MS metal surface.

The low intensity of FT-IR spectra having broad peak at 3353 $cm^{-1}$ indicates an interaction between free –OH with charged metal surface. The characteristic vibrational peak at 629 $cm^{-1}$ is attributed to the metal-oxygen (functional group) bond. The peak at 2124 $cm^{-1}$ is mainly due to the presence of $-C\equiv C-H$ (terminal alkyne) and the disappearance of this peak indicates that the π-electrons of inhibitor molecule are also involved in the bonding on the metal surface. These shifting in the absorption frequencies clearly indicate that one or more phytochemicals of inhibitor are adsorbed on the MS surface.

The inhibitive action of CCWL extract on MS in corroding medium is attributed to the adsorption of the components for example, cyclohaxanol derivative containing oxygen atoms in functional groups (-OH) and butanoic acid through C=C. A molecule of small size as cyclohexanol derivative is readily diffused.

In acidic medium these compounds exist as protonated species, which interact with charged metallic surface. Potentiodynamic polarisation curves indicate that these inhibitor molecules retard the corrosion by controlling both anodic and cathodic processes. Protonated molecules adsorb on cathodic sites of MS to retard $H_2$-evolution process, whereas π-system adsorb on anodic sites of MS to prevent the diffusion of metal ions into aqueous phase.

### 4.3. Corrosion Inhibition Studies using Elsholtzia communis (ECI) Extract

The data obtained from the GC-MS analysis of the ECI extract indicates the presence of major phytochemicals in methanolic extracts of ECI such as (-)-spathulenol, β carotene, retinoic acid and retinol acetate as carotenoids derivatives.

The weight loss result clearly indicates the effect of ECI extract on the $C_{rate}$ and there is a significant decrease as the concentration of ECI extract increased. This was due to increase in the extent of adsorption of inhibitors from ECI extract to the MS surface in 1 N HCl medium. The obtained standard free energy values are around -15 kJ/mol and generally the less negative value of standard free energy around (– 20 kJ/mol) are usually characteristic of physical adsorption.

The increase in the corrosion rate with an increase in temperature is due to the desorption of the inhibitor molecules and the adsorption at higher temperature indicated to physical adsorption of inhibitor onto the MS surface. The higher value of $E_a$in presence of ECI extract solution suggests that physical adsorption of inhibitor molecules and formation of physical barrier at MS surface/solution interface.

The positive value of $\Delta H_a$ indicates that the corrosion process is endothermic in nature while a negative correlation was found between the values of $\Delta S_a$ and the concentration of inhibitor in corrosive medium. The higher values of $\Delta S_a$ for inhibition solution are due to increase in entropy of solvent.

The Tafel polarization curves decreases both for anodic and cathodic $I_{corr}$ for all investigated concentrations and the displacement of $E_{corr}$ was around 66 mV towards the cathodic direction with respect to the blank, which showed the inhibitive effect of examined inhibitor. It concludes that inhibitor is of mix type. The $\beta_c$ value was shifted toward more negative side of $E_{corr}$ value, whereas $\beta_a$ was slightly shifted toward lower $E_{corr}$ side.

The EIS data clearly indicates that the value of $C_{dl}$ decreases whereas the value of $R_{ct}$ increases with inhibitor concentration in presence of larger amount of green inhibitor. The decrease in $C_{dl}$ values is interpreted as either strengthening in inhibitive film onto the metal surface i.e., increase in thickness of the electrical double layer or decrease in dielectric constant of the solution or both.

The FT-IR spectra of ECI extract of corrosion product obtained by scratching from the MS surface showed a weak vibrational band of –OH at 3370 $cm^{-1}$ This is probably due to formation of thin film of Fe-inhibitor complex on to the MS surface through –OH group of Retinoic acid or Spathulenol. Disappearance of bands near 1114 and 647 $cm^{-1}$is due to the physiosorption of inhibitor molecules onto the MS surface through the C-O-C, COO-, C=C and -C=C-H groups.

The interaction between organic molecules present in methanolic extract of ECI is attributed as charge-transfer-type interaction between unshared electron pairs present in oxygen in carotenoids derivative or π-electrons of carotenoids and empty low energy d- orbitals of Fe atom present on MS surface and columbic interactions between aromatic π-clouds and MS surface/solution interface or between protonated β-carotenoids and adsorbed $Cl^-$ ions at cathodic sides.

## 4.4. Corrosion Inhibition Studies using Melocanna baccifera (MBL) extract

Weight loss results for MS in 1 N HCl for MBL extract revealed the increase in inhibition efficiency with the increase in MBL extract concentrations which eventually decreasethe corrosion rate. This behaviour is due to the increase in surface area covered by the adsorbed molecules on the MS surface with an increase in MBL extract concentrations having a maximum efficiency of 93% as is achieved at the concentration of 0.5 g/L.

Inhibition of MS corrosion in 1 N HCl in presence of crude extract was attributed due to the adsorption of the phytochemical constituents such as 3-deoxy-d-mannoic lactone and 2,3-dihydroxypropanal of the extract of bamboo leaves on the MS surface and forming a protective layer. Phytochemical screening of different species of bamboo reveals that the extract contains alkaloids, tannins, general glycosides, saponnins, coumarins, alkaloids, flavonoids, anthraquinones and anthracene glycoside. These functional groups along with hetero-atoms such as nitrogen, oxygen, and multiple bonds in their molecule possesses higher electron density and hence facilitates in forming the coordinate bond with metal d-orbitals.

It is also observed from the polarization curves that addition of the inhibitors affected both the anodic and cathodic processes as the curves are shifted towards lower corrosion current density region with respect to the blank. This is due to inhibitor molecules inhibit both anodic and cathodic corrosion process of electrode in electrolytic solution.

The shifts in corrosion current densities appear to be more dominant for the anodic curves than the cathodic curves. This suggests that the inhibitor suppressed predominantly the anodic reaction than the cathodic reaction. These results suggest that inhibitor molecules are adsorbed on metal surface and retarded the electrodes processes. This is considered due to the mixed-type behaviour of the studied inhibitors. The obtained inhibitors efficiency by electrochemical method is also supported by weight loss method.

The -OH vibrational band at 3200-3470 $cm^{-1}$ of the MBL spectrum in Figure 3.4.6 was shifted to 3300-3500 $cm^{-1}$ in the spectrum of the MBL-metal complex. The C=O stretching frequency of MBL extract shifts from 1545 $cm^{-1}$ to 1474 $cm^{-1}$. This indicates the participation of the heteroatoms of inhibitor molecule on metal surface.

### 4.5. Corrosion Inhibition Studies using Spilanthes acmella (SA) extract

The results of GC/MS revealed that the compounds hexadecanoic acid, hepta-9,10,11-trienoic acid, octadecenoic acid, 5-hydroxylmethyl heptadecane, docosane aldehyde, methyl 11,14,17-eicosatrienoate and 1-thoxyoctadecane are major components present with SA extract.

The gravimetric results indicated the rapid decrease in corrosion rate with increase in SA extract concentrations. This is due to fact that more inhibitor molecules are adsorbed on the MS surface, which protects MS surfaces from aggressive acidic medium. The corrosion rate of MS in 1 N HCl is observed as 4.36 $mg/cm^2/h$ which decreases to 0.41 $mg/cm^2/h$ in presence of 0.5 g/L of SA extract with 90% surface coverage over MS. Further, increase in temperature caused to decrease the corrosion inhibition process.

The Langmuir adsorption isotherm is fitted well in the present system which indicates the monolayer coverage of adsorbed molecules onto the MS surface and no lateral interactions are involved between the adsorbed molecules.

The value of standard free energy was found to be less than −20 kJ/mol. The negative value of standard free energy is due to the electrostatic interactions occurred between the inhibitor molecules and metal surface. Thus, the obtained value of standard free energy suggests a physical adsorption on the MS surface in acidic solution.

The polarisation curve was shifted to more negative and more positive potentials with respect to the blank polarisation curve, by increasing the concentration of Spilanthes acmella extract. These observations indicate that the Spilanthes acmella is a mixed-type inhibitor for the corrosion of MS. It is also noted that the cathodic polarization curves slightly shifted toward negative region, whereas anodic polarisation curve shifted toward greater extent, which means that the inhibition of corrosion reaction predominates with inhibitive anodic dissolution reaction in acidic medium.

It is also seen that the presence of SA extract enhances the values of $R_{ct}$. The increase in $R_{ct}$ is due to the adsorption of SA extract on metal surface which is exposed in corrosive medium and forming a protective film. The intact protective thin film acts as a barrier for intimate interaction of water, oxygen and corrosive anions on the metal surface. All Nyquist plots exhibit one single capacitive loop, indicating the corrosion of MS in 1 N HCl with and without protection is mostly controlled by charge transfer process and double layer capacitance. The low $C_{dl}$ values at higher concentration of SA extract are associated with slower corroding processes, which decreases with local dielectric constant and causes an increase in the thickness of the electrical double layer.

The FT-IR spectra of the SA extract and corrosion product in presence of inhibitor shows that active functional groups such as C=C, C=O or O-H is associated with bonding onto iron metal surface.

The morphology (SEM image) of the MS with SA extract shows significant difference from the blank MS without inhibitor in acidic solution. The extent of rough surface formed on metal surface is reduced due to the adsorptions of inhibitor molecules.

The corrosion inhibition of MS is due to the adsorption of unsaturated fatty acid derivative phyto-constituents present in SA extract. Inspection of the structure of present compound reveals that the π bonds almost protected the metal and protonated oxygen atoms are involved in the formation of protective layer on the metal surface. Therefore, high inhibition efficiency is obtained relatively at lower concentrations of the SA extract.

## 4.6. Future Work

The present study is to be taken as a starting point for the corrosion inhibition study using plant extracts. The study already established the plant extract as effective corrosion inhibitive agent but application of only few of them was explored. The entire natural products derived from plants are important from biological, as well as organo-metallic-chemistry point of view.

Limited number of plant extract are used in metal protection and recognised as corrosive inhibition in acid medium. It is also explored the main phytochemical constituent compounds present in plant extract which are involved in bonding with metal surface.

Further, large quantities of particular phyto-organic compounds using the established methodology is an important aspect to be explored. The particular phytochemical is expected to be important from biological, chemical and other industrial point of view.

Methodology for anti-corrosive studies is established which may further be commercialized for greater implications. The efficient inhibitor was tested as good alternatives for organic substances by comparing the structures of the inhibitors with that of encapsulated coating. An application of natural inhibitors for prevention from crevice, intergranular, and stress corrosion processes could be investigated. New techniques need to be employed for the interpretation of corrosion and inhibition mechanisms. Surface analysis could be conducted with the help of new analytical techniques, which contributes to provide better understanding of inhibition processes in different corrosive medium.

Abbe, B., (1994). The expanding array of environmentally improved new use products from America's farms. Paper presented at New Uses Council's 1994 Agriculture Summit on New Uses, June 21-22, Washington, D.C.

Abboud, Y., Abourriche, A., Ainane, T., Charrouf, M., Bennamara, A., Tanane, O., Hammouti, B., (2009). Corrosion inhibition of carbon steel in acidic media by bifurcaria bifurcate extract. Chem. Eng. Commun., 196:788-800.

Adamaszek, K., Jurasz, Z., Swadzba, L., Grzesik, Z., Mrowec, S., (2007). High Temperature Materials and Processes, 26: 115–122.

Adejoro, I.A., Ojo F.K., Obafemi S.K., (2015). Corrosion inhibition potentials of ampicillin for mild steel in hydrochloric acid solution, Journal of Taibah University for Science, 9: 196–202.

Ahmed, I., (1993). Industrial utilization of agricultural materials: Energy, economic and environmental benefits of bioprocessing. Fourteenth capital metals and materials forum, agricultural commodities: competing with traditional metals and materials, Bureau of Mines and the Department of the Treasury. Oct. 21, Washington, D.C., U.S.

Akdogan, A., Eker, B., (2000). The effect of corrosion on agricultural machinery and prevention methods. Denizli Material Congress. Denizli, Turkey.

Aljourani, J., Raeissi, K., Golozar, M. A., (2009). Benzimidazole and its derivatives as corrosion inhibitors for mild steel in 1M HCl solution., Corros. Sci., 51:1836-1843.

Aljourani, J., Golozar, M. A., Raeissi, K., (2010). The inhibition of carbon steel inhibition of carbon steel corrosion inhydrochloric and sulphuric acid media using some benzimidazole derivatives. Materials Chemistry and Physics, 121(1): 320-325.

Ali, A. I., Mahrous Y. S., (2017). Corrosion inhibition of C-steel in acidic media from fruiting bodies of Melia azedarach L extract and a synergistic $Ni^{2+}$ additive. RSC Adv., 7: 23687–23698.

Anantharaman, T.R., (1996). The Rustless Wonder—A Study of the Iron Pillar at Delhi. New Delhi, India: Vigyan Prasar, 11–87.

Antos, G.J., Aitani, A.M. (eds)., (2004). Catalytic naphtha reforming. 2nd edn. Marcel Dekker. New York.

Anonymous, Corrosion control of agricultural equipment and buildings, http://www.npl.co.uk/ncs/docs.

Arenas, T.L., Rathi, P., Ramirez-Jimenez, R., Sales-Cruz, M., (2010). Factors affecting the acid pretreatment of lignocellulosic biomass: batch and continuous process. In: Pierucci S, Ferraris B, editors. In: 20th European symposium on computer aided process engineering-ESCAPE.

Aribo, S., Olusegun, S.J., Ibhadiyi L.J., Oyetunji A., Folorunso, D.O., (2016). Green inhibitors for corrosion protection in acidizing oilfield environment. Journal of the Association of Arab Universities for Basic and Applied Sciences. http://dx.doi. org/ 10.1016/ j.jaubas. 2016.08.001.

Asrar, N., Mackay, B., Birketveit, O., Stipanicev, M., Jackson, J.E., Jenkins, A., Melot, D., Scheie, J., Vittonato, J., (2016). Corrosion the longer war, Schlumberger. Oilfield Review, 28:2.

Ating, E.I., Umoren S.A., Udousoro I.I., Ebenso, E.E., Udoh, A.P., (2010). Leaves extract of Ananas sativum as green corrosion inhibitor for aluminium in hydrochloric acid solutions. Green Chemistry Letters and Reviews, 3(2): 61-68.

Avci, G., and Keleş, Y. (2011). Aqueous extract of Acacia cyanophylla leaves as environmentally friendly inhibitor for mild steel corrosion in 1 M H2SO4 solution. Surface and Interface Analysis, 43: 1311–1317.

Awad, H.S, Gawad,S.A., (2005). Mechanism of inhibition of iron corrosion in hydrochloric acid by pyrimidine and series of its derivatives. Anti-Corrosion Methods and Materials, 52(6): 328-336.

Bai, L., Feng, L., Wang, H., Lu Y., Lei X., Bai, F. (2015). Comparison of synergistic effect of counterions on corrosion inhibition of mild steel in acid solution: electrochemical, gravimetric and thermodynamic studies. RSC Adv., 5: 4716-4726.

Balasubramaniam, R., (2000). On the corrosion resistance of the Delhi iron pillar, Corros. Sci., 42: 2103 – 2129.

Balasubramaniam, R., (2002). Delhi iron pillar-New insights. Shimla, India: Indian Institute of Advanced Study, 3–88.

Balasubramaniam, R., Saxena A., Anantharaman T. R., Reguer S., Dillmann P., (2004). A marvel of medieval Indian metallurgy: Thanjavur’s forge-welded iron cannon. JOM., 56(1): 17–23.

Bardal, E., (2004). Corrosion and Protection, Springer-Verlag. London.

Balandrin, M., Klocke, J., Wurtele, E., Bollinger, W., (1985). Natural plant chemicals: sources of industrial and medicinal materials. Science, 228(4704): 1154–1153.

Bammou, L., Belkhaouda, M., Salghi, R., Benali, O., Zarrouk, A., Zarrok, H., Hammout, B., (2014). Corrosion inhibition of steel in sulfuric acidic solution by the chenopodiumambrosioides extracts L. Journal of the Association of Arab Universities for Basic and Applied Sciences, 16: 83–90.

Barry, W.P., James, D.F., Robert, M.K., Stanley, J.P., (2000). The Influence of iron contamination on the corrosion resistance of several stainless steels. Corrosion, 26-31.

Bayol, E., Gurten, A.A., Dursun, M., Kayakirilmaz, K., (2008). Adsorption behavior and inhibition corrosion effect of sodium carboxymethyl cellulose on mild steel in acidic medium. Acta Physico Chimica Sinica, 24(12): 2236-2243.

Behera, S., Arora, R., Nandhagopal, N., Kumar, S., (2014). Importance of chemical pretreatment for bioconversion of lignocellulosic biomass. Renewable and Sustainable Energy Reviews, 36: 91–106.

Behpour, M., Ghoreishi, S. M., Khayatkashani, M., Soltani, N. (2012). Green approach to corrosion inhibition of mild steel in two acidic solutions by the extract of Punica granatum peel and main constituents. Materials Chemistry and Physics, 131: 621–633.

Behpour, M., Ghoreishi, S. M., Mohammadi, N., Soltani, N., Salavati-Niasari, M., (2010). Investigation of some schiff base compounds containing disulfide bond as HCl corrosion inhibitors for mild steel. Corros. Sci., 52: 4046–4057.

Behpour, M., Ghoreishi, S.M., Khayatkashani, M., Soltani, N., (2011). The effect of two oleo-gum resin exudates from Ferulaassa-foetida and Dorema ammoniacum on mild steel corrosion in acidic media. Corros. Sci., 53: 2489–2501.

Benali, O., Selles, C., Salghi, R. (2014). Inhibition of acid corrosion of mild steel by Anacyclus pyrethrum L. extracts. Research on Chemical Intermediates, 40: 259–268.

Benmenine, A. E. K., Ouahrani, M. R., Gherraf, N., Sekirifa, M. L., Baameur, L. (2014). Anticorrosive action study of Retama retam extracts on mild steel X52 in 20% $H_2SO_4$ solution. Energy Procedia, 50: 401–405.

Beukenberg, M., (2006). In proceedings of turbine forum 2006. Advances coatings for high temperatures. Turbine forum. Nice. 2006. April 26–28.

Bijker, W.E., Hughes, T.P., Pinch, T., (eds) (1987). The social construction of technological systems, new directions in the sociology and history of technology. MIT, Cambridge.

Bin, X., Wenzhong, Y., Ying, L., Xiaoshuang, Y., Weinan, G., Yizhong, C., (2014). Experimental and theoretical evaluation of two pyridine carboxaldehyde thiosemicarbazone compounds as corrosion inhibitors for mild steel in hydrochloric acid solution. Corros. Sci., 78: 260–268.

Biswas, A.K., (1999). Minerals and Metals in Medieval India,” History of Indian Science, Technology and Culture, A.D. 1000-1800, ed. A. Rahman. New Delhi, India: Oxford University Press, 275–313

Bhardwaj S., Gakhar S.K., (2005). Ethnomedicinal plants used by the tribals of Mizoram to cure cuts and wounds. Indian Journal of Traditional Knowledge, 4(1): 75-80.

Bommersbach, P., Alemany-Dumont, C., Millet, J.P., Normand, B., (2005). Formation and behaviour study of an environment-friendly corrosion inhibitor by electrochemical methods, Electrochim. Acta, 51: 1076-1084.

Boothroyd, G., Knight, W.A., (1989). Fundamentals of machining and machine tools. 2nd edn. Mercel Decker, New York

Bradford, S.A. (1993). Cathodic and Anodic Protection. In: Corrosion Control. Springer, Boston. MA.

Brett, C.M.A., Melo, P.I.C., (1997). Influence of anions on the corrosion of high speed steel. J. Applied Electrochemistry, 27: 959-964.

Broadbent, C., (2016). Steel's recyclability: demonstrating the benefits of recycling steel to achieve a circular economy, Int. J. Life. Cyc. Ass., 21: 1658–1665.

Brodeur, G., Yau, E., Badal, K., Collier, J., Ramachandran, K.B., Ramakrishnan, R., (2011). Chemical and physioco chemical pre-treatment of lignocellulosic biomass: a review. Enz Res. http://dx.doi.org/10.4061/2011/787532.

Broughton, E., (2005). The Bhopal disaster and its aftermath: A review. Environ. Health. 4: 6. doi: 10.1186/1476-069X-4-6

Bungay, H. R., (1981). Energy. The biomass options. John Wiley and Sons. New York.

Burns, R.M., Bradley, W.W., (1955). Protective coatings for metals. American chemical society monograph 129. Van Nostrand Reinhold Company. New York.

Carbon steel versus stainless steel the differences matter more than you think, (2017). www. reliance-foundry.com/blog/carbon-steel-versus-stainless-steel#gref.

Cardozo da Rocha, J., da Cunha Ponciano Gomes, J. A., D'Elia, E. (2010). Corrosion inhibition of carbon steel in hydrochloric acid solution by fruit peel aqueous extracts. Corros Sci., 52: 2341–2348.

Carlsten, C., (2003). The Bhopal disaster: prevention should have priority now. Int. J. Occup Environ Health, 9(1): 93-94.

Cedeño M.L., Vera L. E., Pineda T. Y., (2017). A study of corrosion inhibition of steel AISI-SAE 1020 in $CO_2$- brine using surfactant Tween 80. Journal of Physics: Conf. Series,786: 012038.

Chai, C., Xu,Y., Shi, Zhao, S. X., Wu, Y., Xu ,Y., Zhang, L., (2018). Functional polyaspartic acid derivatives as ecofriendly corrosion inhibitors for mild steel in 0.5 M $H_2SO_4$ solution. RSC Adv., 8: 24970–24981.

Chaitra, T.K., Mohana, K.N., Tandon, H. C., (2017). Comparative study of Levofloxacin and its amide derivative as efficient water soluble inhibitors for mild steel corrosion in hydrochloric acid solution. Int. J. Ind. Chem., 8: 1–15.

Chakravarthy, M. P., Mohana, K. N., Kumar, C. B. P., (2014). Corrosion inhibition effect and adsorption behaviour of nicotinamide derivatives on mild steel in hydrochloric acid solution. Int. J. Ind. Chem., 5: 19. https://doi.org/10.1007/s40090-014-0019-3.

Challouf, H., Souissi, N., Messaouda, M.B., Triki, E., Abidi R., (2013). A correlation between malva sylvestrisextracts molecules and their corrosion inhibition capabilities. Surface Engineering and Applied Electrochemistry, 49(4): 320–325.

Chaubey, N., Yadav, D.K., Singh, V.K., Quraishi, M.A., (2015). A comparative study of leaves extracts for corrosion inhibition effect on aluminium alloy in alkaline medium, Ain Shams Eng J., http://dx.doi.org/10.1016/j.asej.2015.08.020.

Chen, H.J., (2000). High temperature corrosion inhibition performance of imidazoline and amide. Corrosion. Paper No. 00035.

Christensen, P. A.; Hamnett, A., (1994). Techniques and mechanisms in electrochemistry. Blackie Academic and Professional. Bishopbriggs. Glasgow. NZ.

Clydesdale, F.M., Ho, C-T, Lee, C.Y., Mondy, N.I., Shewfelt, R.L., Lee, K., (1991). The effects of postharvest treatment and chemical interactions on the bioavailability of ascorbic acid, thiamin, vitamin A, carotenoids, and minerals. CRC Crit. Rev. Anal. Chem., 30:5 99–638.

Coffie, G.Y., Antwi-Boasiako, C., Darkw, N.A., (2014). Phytochemical constituents of the leaves of three bamboo (Poaceae) species in Ghana. Journal of Pharmacognosy and Phytochemistry, 2(6): 34-38.

Corrosion: Understanding the basics. 2000 ASM International. Materials park, Ohio, USA. www.asminternational.org.

Corrosion Technical Bulletin CTB 24 BlueScope steel. www.steel.com.au /media/ Files/ Technical Bulletin/CTB-24.ash.

Coskun, O., (2016). Separation techniques: Chromatography. North Clin Istanbul, 3(2): 156–60.

Czaplicki, S., (2013). Chromatography in bioactivity analysis of compounds. Bioactivity analysis of compounds. http://dx.doi.org/10.5772/55620.

Dai, J., Mumper, R.J., (2010). Plant phenolics: extraction, analysis and their antioxidant and anticancer properties. Molecules, 15: 7313-752.

de la Fuente D., Díaz I., Simancas J., Chico B., Morcillo, M., (2011). Long-term atmospheric corrosion of mild steel. Corros. Sci., 53:604–617.

Deng. S., Li X., Xie X., (2014). Hydroxymethyl urea and 1.3-bis(hydroxymethyl) urea as corrosion inhibitors for steel in HCl solution. Corros. Sci., 80: 276-289.

Deyab, M.A., (2014). Adsorption and inhibition effect of Ascorbyl palmitate on corrosion of carbon steel in ethanol blended gasoline containing water as a contaminant. Corros Sci., 80: 359-365.

Deyab, M.A., (2015). Egyptian licorice extract as a green corrosion inhibitor for copper in hydrochloric acid solution. Journal of Industrial and Engineering Chemistry, 22: 384-389.

Deyab, M.A., (2016). Inhibition activity of Seaweed extract for mild carbon steel corrosion in saline formation water. Desalination, 384: 60–67.

Deyab, M.A., Osman, M.M., Elkholy, A.E., Heakel, F.El-Taib (2017). Green approach towards corrosion inhibition of carbon steel in produced oilfield water using lemongrass extract. RSC Adv., 7, 45241-45251.

Dhanani, T., Shah, S., Gajbhiye, N.A., Kumar, S., (2017). Effect of extraction methods on yield, phytochemical constituents and antioxidant activity of Withania somnifera.Arabian Journal of Chemistry, 10(1): S1193-S1199.

Dixit U.S. et al., (2017). A brief history of mechanical engineering, Materials Forming, Machining and Tribology, DOI 10.1007/978-3-319-42916-8-2. Springer International Publishing Switzerland.

Donohoe, M., (2003). Causes and health consequences of environmental degradation and social injustice. Social Science and Medicine, 56: 573–587.

Dwivedi, D., Lepková, K., Becker T., (2017). Carbon steel corrosion: a review of key surface properties and characterization methods. RSC Adv., 7: 4580-4610.

Eddy, N.O., Odoemelam, S.A., (2009). Inhibition of corrosion of mild steel in acidic medium using ethanol extract of aloe vera. Pigment and Resin Technology, 38(2): 111-115.

Eddy, N.O., Ebenso, E.E., (2008). Adsorption and inhibitive properties of ethanol extracts of Musa sapientum peels as a green corrosion inhibitor for mild steel in $H_2SO_4$. Afr. J. Pure Appl. Chem., 2: 46–54.

El-Etre, A.Y., Abdallah, M., (2000). Natural honey as corrosion inhibitor for metals and alloys. II. C-steel in high saline water. Corros. Sci., 42: 731-738.

El-Etre, A.Y., Abdallah, M., El-Tantawy, Z.E., (2005). Corrosion inhibition of some metals using lawsonia extract. Corros. Sci; 47: 385–395.

El-Haddad, M. N., (2016). Inhibitive action and adsorption behaviour of cefotaxime drug at copper/hydrochloric acid interface: electrochemical, surface and quantum chemical studies. RSC Adv., 6:57844–57853.

Finn, M.E., (1989). Metals handbook: machining.16(9th edn.) ASM International. Ohio.

Foley, R.T., (1970). Role of the chloride ion in iron corrosion. Corrosion, 26(2): 58-70.

Fontana, M.G., Greene N.D., (1986). Corrosion Engineering. McGraw-Hill. New York.

Fouda, A. S., Shalabi, K., Idress, A. A., (2015). Ceratonia siliqua extract as a green corrosion inhibitor for copper and brass in nitric acid solutions. Green Chem. Lett. Rev., 8:17–29.

Gadiyar, H.S., Das, C., Gaonkar, K.B., (1991). Chemical cleaning, decontamination and corrosion. Bhabha atomic research centre. Bombay. India.

Gadow, H. S., Motawea, M. M., (2017). Investigation of the corrosion inhibition of carbon steel in hydrochloric acid solution by using ginger roots extract. RSC Adv., 7: 24576–24588.

Gadow, H. S., Motaweab, M. M., Elabbasy, H. M., (2017). Investigation of myrrh extract as a new corrosion inhibitor for a-brass in 3.5% NaCl solution polluted by 16 ppm sulphide. RSC Adv., 7: 29883-29898.

Garcia-Arriaga, V., Alvarez-Ramirez, J., Amaya, M., Sosa, E., (2010). H2S and O2 influence on the corrosion of carbon steel immersed in a solution containing 3 M diethanolamine. Corros. Sci., 52: 2268–2279.

Gao, X., Zhao, C., Lu, H., Gao, F., Ma, H., (2014). Influence of phytic acid on the corrosion behavior of iron under acidic and neutral conditions. Electrochimica Acta, 150: 188–196.

Garcia-Serna, J., Perez-Barrigon, L., Cocero, M.J., (2007). New trends for design towards sustainability in chemical engineering: Green engineering. Chemical Engineering Journal, 133: 7–30.

Garai, S., Garai, S., Jaisankar, P., Singh, J.K. Elango, A., (2012). A comprehensive study on crude methanolic extract of Artemisia pallens (Asteraceae) and its active component as effective corrosion inhibitors of mild steel in acid solution. Corros. Sci., 60: 193-204.

Geethamani, P., Kasthuri, P.K., (2015). Adsorption and corrosion inhibition of mild steel in acidic media by expired pharmaceutical drug. Cogent Chemistry 1: 1091558 http://dx.doi.org/10.1080/23312009.2015.1091558.

Gomez-Caravaca, A.M.., Verardo, V., Segura-Carretero, A., (2008). Development of a rapid method to determine phenolic and other polar compounds in walnut by capillary electrophoresis-electrospray ionization time of flight mass spectrometry. J Chroomatogr., A1209: 238-245.

Gopi, G.K.M.D., Kavitha, L. (2009). Inhibiting effects of 4-amino-antipyrine based schiff base derivatives on the corrosion of mild steel in hydrochloric acid. Journal of Applied Electrochemistry, 39(12): 2345-2352.

Graedel, T.E., Allenby, B.R., (1995). Industrial Ecology. Prentice Hall, Englewood.

Groysman, A., (2014). Corrosion in Systems for Storage and Transportation of Petroleum Products and Biofuels. Springer. Dordrecht.

Groysman, A., (2010). Corrosion for Everybody. Springer. Dordrecht.

Grubler, A., (1998). Technology and Global Change. Cambridge Univ. Press. Cambrigde.UK.

Grzesik, Z., Smoła, G., Adamaszek, K., Jurasz, Z., Mrowec, S., (2013). Thermal shock corrosion of valve steels utilized in automobile industry. Oxid Met., 80: 147–159.

Grzesik, Z., Mrowec, S., Jurasz, Z., Adamaszek, K., (2010). High temperature materials and processes, 29: 35–45.

Gundry, R.D. (1993). Corrosion. Plenary and Keynote Lectures. NACE International Houston: TX,

Guo, L., Zhang S. T., Li, W. P., Hu G., Li, X. (2014). Experimental and computational studies of two antibacterial drugs as corrosion inhibitors for mild steel in acid media. Materials and Corrosion, 65(9): 935-942.

Gupta, N.K., Quraishi, M. A., Verma, C., Mukherjee, A. K., (2016). Green schiff's bases as corrosion inhibitors for mild steel in 1 M HCl solution: experimental and theoretical approach. RSC Adv., 6: 102076-102087.

Gupta, R.K., Malviya, M., Verma, C., Gupta, N.K., Quraishi, M.A., (2017). Pyridine-based functionalized graphene oxides as a new class of corrosion inhibitors for mild steel: an experimental and DFT approach. RSC Adv., 7: 39063-39074.

Gutzeit, J, Merrick, R.D., Scharfstein, L.R., (1987). Corrosion in petroleum refining and petrochemical operations. In: Corrosion. ASM Handbook, ASM International. 13: 1262–1287.

Halambek, J., Berković, K., Vorkapić-Furač J., (2010). The influence of Lavandula angustifolia L. oil on corrosion of Al-3Mg alloy. Corros Sci.,., 52( 12) : 3978-3983.

Haldhar, R., Prasad, D., Saxena, A., Singh , P., (2018). Valeriana wallichii root extract as a green and sustainable corrosion inhibitor for mild steel in acidic environments: experimental and theoretical study, Mater. Chem. Front., 2:1225-1237.

Hazarika, T.K., Nautiyal, B.P., (2012). Studies on wild edible fruits of Mizoram, India used as ethno-medicine. Genetic Resources and Crop Evolution, 59(8): 1767-1776.

Hazarika, T.K., Marak, S., Mandal, D., Upadhyaya, K., Nautiyal, B.P., Shukla, A.C., (2016). Underutilized and unexploited fruits of Indo-Burma hot spot, Meghalaya, north-east India: ethno-medicinal evaluation, socio-economic importance and conservation strategies. Genetic Resources and Crop Evolution, 63(2): 289-304.

Harmsen, P., Huijgen, W., Bermudez-Lopez L., Bakker, R., (2010). Literature review of physical and chemical pretreatment processes for lignocellulosic biomass, 1st ed. Wageningen: Food and Biobased Research.

Hamdy, A., El-Gendy, N.S., (2013). Thermodynamic, adsorption and electrochemical studies for corrosion inhibition of carbon steel by henna extract in acid medium. Egyptian Journal of Petroleum, 22: 17–25.

Hasyim, M.R., Ma, D., Rajagopalan, R., Randalle, C., (2017). Prediction of charge discharge and impedance characteristics of electric double layer capacitors using porous electrode theory. Journal of the Electrochemical Society, 164(13): A2899-A2913.

Heitz, E., (1974). Corrosion of Metals in Organic Solvents; New York: Plenum Press.

Heitz, E., Henkhaus, R., Rahmel, A., (1992). An experimental approach. Corros. Sci., Ellis Horwood. Chichester. England.

Hernández, A.R., Contreras, O.C., Acevedo, J.C., Moreno, L.G.N.,Poly (ε-caprolactone) degradation under acidic and alkaline conditions. American Journal of Polymer Sci., 3(4): 70-75.

Hegazy, M.A., Abdallah, M., Ahmed, H., (2010). Novel cationic gemini surfactants as corrosion inhibitors for carbon steel pipelines. Corros. Sci., 52: 2897-2904.

Hadorn, G.H., Hoffmann-Riem, H., Biber-Klemm, S., Grossenbacher-Mansuy, W., Joye, D., Pohl, C., Wiesmann, U., Zemp, E., Handbook of Trans disciplinary Research. Springer. Schwarztorstrasse. Bern. Switzerland.

Hosseini, M., Mertens, S.F.L, Ghorbani, M., Arshadi, M.R., (2003). Asymmetrical Schiff bases as inhibitors of mild steel corrosion in sulphuric acid media. Materials Chemistry and Physics, 78(3): 800-808.

Hosseini, S.M.A., Salari, M., Jamalizadeh, E., Khezripoor, S., Seifi, M., (2010). Inhibition of mild steel corrosion in sulfuric acid by some newly synthesized organic compounds. Materials Chemistry and Physics, 119: 100–105.

Hoseizadeh, A. R., Danaee, I., Maddahy, M.H., (2014). Adsorption and corrosion inhibitive properties of 2-Mercaptobenzothiazole on AISI steel 4130 alloy in hydrochloric acid solution. Kovove Mater., 52: 35–45.

Huesemann, M.H., (2001). Can pollution problems be effectively solved by environmental science and technology. An analysis of critical limitations. Ecological Economics, 37: 271–287.

Jack C., (1995). Making Iron and Steel: The Historic processes 1700-1900. Ringwood, North Jersey highlands historical Society. NZ.

Ji, G., Dwivedi, P., Sundaram, S., Prakash, R. (2013). Inhibitive effect of Chlorophytum borivilianum root extract on mild steel corrosion in HCl and H2SO4 solutions. Indus. Eng. Chem. Res. 52: 10673–10681.

Jia, Z., Liu, J., Wang, Q., Li, S., Qi, Q., Zhu, R., (2015).Synthesis of 3D hierarchical porous iron oxides for adsorption of Congo red from dye wastewater. J. Alloy. Comp., 622:587-595.

Johnsirani, V., Sathiyabama, J., Rajendran, S., Christyc, S.M. L, Jeyasundari, J., (2013). The Effect of Eclipta Alba Leaves Extract on the Corrosion Inhibition Process of Carbon Steel in Sea Water. Portugaliae Electrochimica Acta, 31(2): 95-106.

Joyce, I. B., Yves, A., (2013). Current trends in green technologies in food production and processing. Food Eng. Rev., 5:1–17.

Jurasz, Z., Adamaszek, K., Janik, R., Grzesik, Z., Mrowec, S., (2009). High temperature corrosion of valve steels in atmosphere containing water vapor. J. Solid State Electrochem.,13: 1709–1714.

Juttner K., (1990). Electrochemical impedance spectroscopy (EIS) of corrosion processes on inhomogeneous surfaces. Electrochem Acta. 35, 1501–1508 (1990)

Kadhum, A.A.H., Mohamad, A.B., Hammed, L.A., Al-Amiery, A.A., San, N.H., Musa, A.Y., (2014). Inhibition of mild steel corrosion in hydrochloric acid solution by new coumarin. Materials, 7(6): 4335–4348.

Kanematsu, H., Barry, D.M. (2016). The application of corrosion protection. In: Kanematsu H., Barry D. (eds) Corrosion Control and Surface Finishing. Springer, Tokyo, 978-4-431-55957-3.

Kar, A., Bora, D., Borthakur, S. K., Goswami, N. K., Saharia, D., (2013). Wild edible plant resources used by the mizos of Mizoram, India. Kathmandu University Journal of science, engineering and technology, 9(I): 106-126.

Karthik, G., Sundaravadivelu, M., Rajkumar, P., (2015). Corrosion inhibition and adsorption properties of pharmaceutically active compound esomeprazole on mild steel in hydrochloric acid solution. Res. Chem. Intermed., 41: 1543 –1558.

Karthik, G., Sundaravadivelu, M., (2016). Studies on the inhibition of mild steel corrosion in hydrochloric acid solution by atenolol drug. Egyptian Journal of Petroleum, 25(2): 183-191.

Khanra, A., Srivastava, M., Rai, M.P., Prakash, R., (2018). Application of unsaturated fFatty acid molecules derived from microalgae toward mild steel corrosion inhibition in HCl solution: A novel approach for metal−inhibitor association. ACS Omega 2018, 3, 12369−12382.

Khomdram, S.D., Salam, J.S., Singh, P.K., (2011). Estimation of nutritive indices in eight lamiaceae plants of Manipur. American journal of food technology, 6(10): 924-931.

Kim, W., Kim, J., Veriansyah, B., Kim, J., Lee, Y., Oh, S., Tjandrawinata, R., (2009). Extraction of bioactive components from Centella asiatica using subcritical water. J. Supercrit. Fluid, 48(3): 211–217.

Kim, Y.S., Kim, J.G., (2017). Evaluation of corrosion fatigue and life prediction of lower arm for automotive suspension component. Met. Mater. Int., 23(1): 98-105.

Krishnan, M., Subramanian, H. Dahms, H-Uwe, Sivanandham,V., Seeni, P., Gopalan, Mahalingam, S. A., Rathinam, A.J., (2018) .Biogenic corrosion inhibitor on mild steel protection in concentrated HCl medium. Scientific Reports, 8:2609.

Koch, G.H., Brongers, M.P.H., Thompson, N.G., Virmani, Y.P., Payer, J.H., (2002). Corrosion costs and preventive strategies in the United States. FWHA-RD-01–156. Houston, TX U S. Department of Transportation, Federal Highway Administration.

Koch, G., Varney, J., Thompson, N., Moghissi, O., Gould, M., Payer, J., (2013). International measures of prevention, application, and economics of corrosion technologies study. Houston, TX: NACE International.

Koch, G., Varney, J., Thompson, N., Moghissi, O., Gould, M., Payer, J., (2016). NACE International impact. International measures of prevention application and economic of corrosion technologies study. NACE International. Houstan. Texas. USA.

Koenig, G., Lohmar,E., Rupprich, N., Lison, M., Gnass, A., (2008).Ullmann's encyclopedia of industrial chemistry. 7th ed. John Wiley & Sons. NY.

Kofstad, P., (1988). Development of stresses and strains, non-protective scales, phase boundary reactions in high temperature corrosion. Elsevier Applied Science. London.

Kokalj, A., (2015). Ab initio modeling of the bonding of benzotriazole corrosion inhibitor to reduced and oxidized copper surfaces. Faraday Discuss, 180: 415-438.

Kosari, A., Moayed, M.H., Davoodi, A., Parvizi, R., Momeni, M., Eshghi, H., Moradi, H., (2014) Electrochemical and quantum chemical assessment of two organic compounds from pyridine derivatives as corrosion inhibitors for mild steel in HCl solution under stagnant condition and hydrodynamic flow. Corros. Sci., 78: 138–150.

Kovacs, L., Csupor, D., Lente, G., Gunda, T., (2014). 100 chemical myths misconceptions misunderstanding, explanations. 22: 396.

Kumar, A.V. R., Balasubramaniam, R., (1998) Corrosion product analysis of corrosion resistant ancient Indian iron. Corros. Sci., 40 (7): 1169-1174.

Kumar, S., Vashisht H., Olasunkanmi L.O., Indra B., Verma H., Goyal M., Singh G., Ebenso, E.E., (2017). Polyurethane based triblock copolymers as corrosion inhibitors for mild steel in 0.5 M $H_2SO_4$. Ind. Eng. Chem. Res., 56 (2): 441–456.

Kumari, P. P., Shetty P., Rao S.A., (2017). Electrochemical measurements for the corrosion inhibition of mild steel in 1 M hydrochloric acid by using an aromatic hydrazide derivative. Arabian Journal of Chemistry, 10: 653–663.

Lai G.Y., (1990). High temperature corrosion of engineering alloys. ASM International.

Lamaka, S.V., Zheludkevich, M.L., Yasakau, K.A., Montemor, M.F., Ferreira, M.G.S., (2007). High effective organic corrosion inhibitors for 2024 aluminium alloy. Electrochimica Acta, 52(25): 7231-7247.

Laughlin, Z., Conreen, M., Witchel, H.J., Miodownik, M., (2011). The use of standard electrode potentials to predict the taste of solid metals. Food Quality and Preference, 22: 628–637.

Leena, P., Hukuman, N. H. Z., Biju, A. R., Jisha, M.,(2019). Studies on methanolic extract of Lepidagathis keralensis as green corrosion inhibitor for mild steel in 1M HCl. J. Electrochem. Sci. Technol., 10(2): 231-243.

Lewandowski D.A., (2000). Design of thermal oxidation systems for volatile organic compounds. CRC. LLC Lewis Publishers. Boca Raton.

Lgaz H., Salghi R., Chaouiki A., Shubhalaxmi, Jodeh S., K. Bhat S., (2018). Pyrazoline derivatives as possible corrosion inhibitors for mild steel in acidic media: A combined experimental and theoretical approach. Cogent Eng., 5: 1441585.

Li, J., Fan, T., Xu Y., Wu X., (2016). Ionic liquids as modulators of physicochemical properties and nanostructures of sodium dodecyl sulfate in aqueous solutions and potential application in pesticide microemulsions. Phys. Chem. Chem. Phys., 18: 29797-29807.

Li, L., Xu W., Lei J., Wang, J., He, J., Li N., Pan, F., (2015). Experimental and theoretical investigations of michelia alba leaves extract as a green highly- effective corrosion inhibitor for different steel materials in acidic Solution. RSC Adv., 00:1/3. DOI: 10.1039/x0xx00000x.

Li, X.H., Deng, S.D., Fu, H., (2012). Inhibition of the corrosion of steel in HCl, H2SO4 solutions by bamboo leaf extract. Corros. Sci., 62: 163–175.

Li, X.H., Deng, S.D., Fu, H. (2010). Inhibition by Jasminum nudiflorum Lindl. leaves extract of the corrosion of cold rolled steel in hydrochloric acid solution. J. Appl. Electrochem, 40: 1641–1649.

Li, W., He, Q., Pei, C., Hou, B., (2007). Experimental and theoretical investigation of the adsorption behaviour of new triazole derivatives as inhibitors for mild steel corrosion in acid media. Electrochim Acta, 52: 6386–6394.

Li, W., Woo, O.T., Guzonas, D., Li, J., Huang, X., Sanchez, R., Bibby C.D., (2015). Effect of pressure on the corrosion of materials in high temperature water. In: Carpenter J.S. et al. (eds) Characterization of minerals, metals, and materials. Springer, Cham.

Loto, R.T., Loto, C.A.,(2018). Anti-corrosion properties of the symbiotic effect of Rosmarinus officinalis and trypsin complex on medium carbon steel, Rosmarinus offcinalis, Results in Physics,10: 99-106.

Malko M.W., Wróblewska A., (2016). The importance of R- (+)-limonene as the raw material for organic syntheses and for organic industry. CHEMIK., 70(4): 193–202.

Mansfeld F., Shih H., Greene H., Tsai C. H., (1993). Analysis of EIS data for common corrosion processes in electrochemical impedance analysis and interpretation. ASTM STP 1188.

Maqbool, F., Bahadar, H., Abdollahi, M., (2014). Science for the benefits of all: The way from idea to product. J. Med. Hypo. Ideas, 8: 74–77.

Marimuthu, S., Padmaja, B., Nair, S., (2013). Phytochemical screening studies on Melia orientalis by GC-MS analysis. Pharmacognosy Res., 5(3): 216–218.

Martinez, S., (2003). Inhibitory mechanism of mimosa tannin using molecular modeling and substitutional adsorption isotherms. Materials Chemistry and Physics, 77: 97–102.

Meng,Y., Ning, W. Xu, B., Yang, W., Zhang, K., Chen,Y., Li, L., Liu X., Zhenga J., Zhang Y.,(2017). Inhibition of mild steel corrosion in hydrochloric acid using two novel pyridine Schiff base derivatives: a comparative study of experimental and theoretical results. RSC Adv., 7: 43014–43029.

Miksic, B.M., Furman, A.Y., Kharshan, M.A., (2009). Effectiveness of the corrosion inhibitors for the petroleum industry under various flow conditions. NACE International, Corrosion Conference and Expo.

Mirahmadi, K., Kabir, M.M., Jeihanipour, A., Karimi, K., Taherzadeh, M.J., (2010). Alkaline pretreatment of spruce and birch to improve bioethanol and biogas production. Bioresources, 5(2): 928–38.

Mobin, M., Rizvi. M., Olasunkanmi L.O., Ebenso E.E.,(2017). Biopolymer from tragacanth gum as a green corrosion inhibitor for carbon steel in 1 M HCl Solution. ACS Omega, 2(7): 3997–4008.

Moerman, F., Partington, E. Materials of construction for food processing equipment and services: requirements, strengths and weaknesses. J. Hyg. Eng. Design Review paper, UDC 664.013/.018:006.73.

Moiseeva, L. S., (2005). Carbon dioxide corrosion of oil and gas field equipment. Protection of Metals. 41(1): 76–83.

Moors, E., (2000). Metal making in motion, technology choices for sustainable metals production. Delft University Press. Delft.

Montanari, A., (2015). Basic Principles of Corrosion of Food Metal Packaging. In: Food Packaging Hygiene. Springer Briefs in Molecular Science. Springer, Cham.

Montemor, M.F. (2016). Fostering Green Inhibitors for Corrosion Prevention. In: Hughes A., Mol J., Zheludkevich, M., Buchheit, R. (eds) Active Protective Coatings. Springer Series in Materials Science, vol. 233. Springer, Dordrecht.

Mourya, P., Banerjee, S., Singh, M.M., (2014).Corrosion inhibition of mild steel in acidic solution by Tageteserecta (Marigold flower) extract as a green inhibitor, Corros. Sci., 28: 352-363.

Mrowec S., Weber T., (1982). Scaling-resistant iron-base alloys in modern scaling-resistant materials. National bureau of standards and national science foundation. Washington D.C.

Mulder K. F., (2007). Innovation for sustainable development: from environmental design to transition management. Sustain. Sci., 2: 253–263.

Muthukrishnan, P., Prakash, P., Jeyaprabha, B., Shankar, K., (2015). Stigmasterol extracted from ficushispida leaves as a green inhibitor for the mild steel corrosion in 1 M HCl solution. Arabian Journal of Chemistry. http:// dx.doi.org/ 10.1016/ j.arabjc.2015.09.005.

Murthy, Z. V. P., Vijayaragavan, K., (2014). Mild steel corrosion inhibition by acid extract of leaves of hibiscus sabdariffa as a green corrosion inhibitor and sorption behaviour. Green Chem. Lett. Rev., 7: 209–219.

Naemnezhad, A., Isari, A.A., Khayer, E., Olya, M. E.B., (2017). Consequence assessment of separator explosion for an oil production platform in South of Iran with PHAST software model. Earth Syst. Environ., 3:43.

Nataraja, S. E., Venkatesha, T.V., Manjunatha, K., Poojary B., Pavithra M. K., Tandon H.C., (2011). Inhibition of the corrosion of steel in hydrochloric acid solution by some organic molecules containing the methylthiophenyl moiety. Corros. Sci., 53: 2651-2659.

Natarajan, K. A., Advances in Corrosion Engineering, NPTEL lecture. IISc Bangalore.

Nath, S.C., Bordoloi, D. N., (1991). Clerodendrum colebrookianum, a folk remedy for the treatment of hypertension in Northeastern India. International Journal of Pharmacognosy, 29(2): 127-129.

Naumenko D., Singheiser L., Quadakkers W. J., (1999). In Proceedings on EFC Workshop. EFC, Frankfurt/Main.

Nešic´S., Sun W., (2010). Corrosion in acid gas solutions, in: J.A.R. Tony (Ed.), Shreir’s Corrosion, Elsevier, Oxford. 1270–1298.

Noor E.A., (2009). Evaluation of inhibitive action of some quaternary N-heterocyclic compounds on the corrosion of Al–Cu alloy in hydrochloric acid. Materials Chemistry and Physics. 114: 533–541.

Norman G. M., Robert B. G., (2006). Sanitary design and construction for food processing. Principles of food sanitation. Food Sci. Texts Series, 257-267.

Nwankwo, H.U., Olasunkanmi, L.O., Ebenso, E.E., (2017). Experimental, quantum chemical and molecular dynamic simulations studies on the corrosion inhibition of mild steel by some carbazole derivatives. Sci Rep., 7: 2436. DOI:10.1038/s41598-017-02446-0.

Obi-Egbedi, N.O., Obot, I.B., (2013). Xanthione: A new and effective corrosion inhibitor for mild steel in sulphuric acid solution. Arabian Journal of Chemistry, 6:211–223.

Oguzie, E.E., (2006). Adsorption and corrosion inhibitive properties as Azadirachta indica in acid solutions. Pigment and resin Technology, 35(6): 334-340

Okafor P.C., Liu X., Zheng Y.G., (2009). Corrosion inhibition of mild steel by ethylamino imidazoline derivative in CO2-saturated solution, Corros. Sci., 51: 761–768.

Okafor, P. C. , Liu, C. B., Zhu, Y. J., Zheng, Y. G., (2011). Corrosion and corrosion inhibition behaviour of N80 and P110 carbon steels in CO2-saturated simulated formation water by rosin amide imidazoline. Ind. Eng. Chem. Res., 50(12):7273–7281.

Osman, M.M., Shalaby, M.N., (2003). Some ethoxylated fatty acids as corrosion inhibitors for low carbon steel in formation water. Mater. Chem. Phys., 77: 261–269.

Ostovari, A., Hoseinieh, S.M., Peikari, M., Shadizadeh, S.R., Hashemi, S.J., (2009). Corrosion inhibition of mild steel in 1 M HCl solution by henna extract: a comparative study of the inhibition by henna and its constituents (lawsone, Gallic acid, a-d-Glucose and Tannic acid). Corros. Sci., 51:1935–1949.

Otto, K., Wood, K., (2001). Product Design: Techniques in reverse engineering and new product development. Pearson Education. Upper Saddle River.

Pan, T. J., Lu, W.M., Ren, Y.J., Wu, W.T., Zeng, C.L., (2009). Electrochemical impedance-spectroscopy (EIS) study of corrosion of steels 12CrMoV and SS304 beneath a molten ZnCl2–KCl film at 400C in air., Oxid Met.,72:179–190.

Pandey, A., Soccol, C.R , Larroche, C., (2008). Current developments in solid-state Fermentation, Springer, New York.

Papavinasam, S., (2000). Corrosion Handbook. (2nd edn), John Wiley & Sons, Inc.

Parekh, K., Jauhari, S., Upadhyay, R.V., (2016). Mechanism of acid corrosion inhibition using magnetic nanofluid, Adv. Nat. Sci. Nanosci. Nanotechnol., 7: 045007.

Patel, K.N., Patel, J.K., Patel, M.P., Rajput, G.C., Patel, H.A., (2010). Introduction to hyphenated techniques and their applications in pharmacy. Pharm Methods, 1(1): 2–13.

Payer, J.H., Boyd, W.K., (1980). Materials Performance. NACE.

Petek, A., Kovačič, S., (2014). The influence of Ce3+ ions on the corrosion rate of stainless steel in acidic solutions of different pH-values. Green Chemistry Letters and Reviews., 7(4): 337–341.

Prabakaran, M., Kim Seung-Hyun , Hemapriya, V., Gopiraman, M. , Kim I.S., Chung Ill-Min., (2016). Rhus verniciflua as a green corrosion inhibitor for mild steel in 1 M $H_2SO_4$. RSC Adv., 6:57144-57153.

Prakash, B., (1991). Metallurgy of iron and steel making and blacksmithy in ancient India. Indian J. History of Sci. 26(4): 351-371.

Prakash, B., (1983). Metallurgy in India through the ages. Bulletin of Metal Museum. 8: 23-26.

Qiang, Y., Guo, L., Zhang, S., Li, W., Yu, S., Tan, J., (2016). Synergistic effect of tartaric acid with 2,6-diaminopyridine on the corrosion inhibition of mild steel in 0.5 M HCl. Scientific Reports. 6:33305. DOI: 10.1038/srep33305.

Raghavendra, N., Bhat, J. I., (2016). Natural Products for material protection: An interesting and efficacious anticorrosive property of dry arecanut seed extract at electrode (Aluminum)–electrolyte (hydrochloric acid) interface. J. Bio. Tribo-Corros., 2:21.

Rahiman, A.F.S.A., Sethumanickam, S., (2017). Corrosion inhibition, adsorption and thermodynamic properties of poly (vinyl alcohol-cysteine) in molar HCl. Arabian Journal of Chemistry, 10: S3358–S3366.

Rahse, W., (2014). Industrial Product Design: Materials for the Machinery. Chem Bio Eng. Rev., 14(3): 1–16.

Rajan, J.P., Singh, K.B., Singh, S., Mishra, R.K., (2014). Trace elements content in the selected medicinal plants traditionally used for curing skin diseases by the native of Mizoram, India. Asian Pac J Trop Med., S410-S414.

Raja, P.B., Sethuraman, M.G., (2008). Natural products as corrosion inhibitor for metals in corrosive media-A review. Material Letters. 62: 113-116.

Ramawat, K.G., (2009). Herbal Drugs: Ethnomedicine to modern medicine. Springer-Verlag Berlin Heidelberg New York.

Ramawat, K.G., Merillon, J.M., (2008). Bioactive molecules and medicinal plants. Springer. Berlin Heidelberg. New York.

Ramírez-Estrada, A., Mena-Cervantes,, V.Y., Elizalde I., Manzo-Robledo A., Zamudio-Rivera, L.S., Nieto-Alvarez D. A., Farelas, F., Hernández-Altamirano, R., (2017).

Development of a zwitterionic compound derived from β-amino acid as green inhibitor for $CO_2$ corrosive environments. ACS Sustainable Chem. Eng., DOI: 10.1021/acssuschemeng.7b02434.

Rao, J. S., (2000). Iron age of ancient India, international symposium on history of machines and mechanisms proceedings HMM. University of Cassino, Italy. 217-224.

Rao, M.N., (2010). High performance stainless steels for critical engineering applications. Transactions of the Indian Institute of Metals, 63(2-3): 221-230.

Ravinder, B. R., Seenayya, G., Reddy, G., (2000). Fermentative production of acetic acid from various pure and natural cellulosic materials by Clostridium lentocellum SG6 T. World J. Micro. Biotech.,16: 507-512.

Reardon A.C., (2011). Metallurgy for the non-metallurgist. Second Edition. ASM International. Ohio. http://www.asminternational.org.

Rist S., Dahdouh-Guebas F., (2006). Ethnosciences-A step towards the integration of scientific and indigenous forms of knowledge in the management of natural resources for the future. Environ. Dev. Sustain., 8: 467–493.

Roessler, K., (1997). The big cannon pipe at Tanjavur. Metal News. 19(1): 1–4.

Romero, I., Ruiz, E., Castro, E., Moya, M., (2010). Acid hydrolysis of olive tree biomass. Chem. Eng. Res. Design, 88: 633–40.

Roy, P., Karfa, P., Adhikari, U., Sukul, D., (2014). Corrosion inhibition of mild steel in acidic medium by polyacrylamide grafted Guar gum with various grafting percentage: Effect of intramolecular synergism. Corros. Sci., 88: 246-253.

Saha, S.K., Dutta, A., Ghosh, P., Sukul, D., (2016).Novel Schiff-base molecules as efficient corrosion inhibor, Priyabrata Banerjee. itors for mild steel surface in 1 M HCl medium: experimental and theoretical approach. Phys. Chem. Chem. Phys., 18: 17898-17911.

Saini, R. K., Shetty, N.P., Prakash, M., Giridhar, P., (2014). Effect of dehydration methods on retention of carotenoids, tocopherols, ascorbic acid and antioxidant activity in Moringa oleifera leaves and preparation of a RTE product. J. Food Sci. Technol., 51(9): 2176–2182.

Salas, B.V., Schorr M., (2012). Environmental and industrial corrosion-practical and theoretical aspects. In Tech Janeza Trdine. Rijeka. Croatia.

Salas, B.V., Wiener, M.S., Stoytcheva, M., Zlatev, R., Beltran, M.C., Corrosion in the food industry and its control. http://cdn.intechopen.com/pdfs/29168/InTech.

Sastri, V. S., (2011). Green corrosion inhibitors: theory and practice. John Wiley and Sons, Inc., Hoboken, New Jersey.

Sethuraman, M.G., Aishwarya, V., Kamal, C., Jebakumar T., (2017). Immanuel Edison Studies on Ervatinine- The anticorrosive phytoconstituent of Ervatamia coronaria. Arabian Journal of Chemistry, 10: S522–S530.

Shreir, L.L., Jarman, R.A., (2000). Corrosion. Volume I. Metal environment reactions, Great Britain.

Shreir, L.L., Jarman, R.A., Burnstein, G.T., (1994). Corrosion. 3rd. Ed., Butterworth Heinemann, Oxford.

Shrivastava, P., (1987). Bhopal: Anatomy of a Crisis. Cambridge. MA. Ballinger Publishing, 184.

Singh, A., Ituen, E.B., Ansari , K.R, Chauhan, _D.S., Quraishi, M.A., (2019). Surface protection of X80 steel using Epimedium extract and its iodide-modified composites in simulated acid wash solution: a greener approach towards corrosion inhibition, New J. Chem., 43: 8527-8538.

Singh, M., Pant, G., Hossain, K., Bhatia, A.K., (2017). Green remediation. Tool for safe and sustainable environment: a review. Appl. Water Sci., 7(6): 2629–2635.

Singh, P., Ebenso, E.E., Olasunkanmi, L.O., Obot, I.B., Quraishi, M.A., (2016). Electrochemical, theoretical, and surface morphological studies of corrosion inhibition effect of green naphthyridine derivatives on mild steel in hydrochloric acid. J. Phys. Chem. C, 120(6): 3408–3419.

Singh, S.K., Mukherjee, A.K., Singh, M.M., (2000). Corrosion behaviour of mild steel in aqueous acetic acid solutions containing different amount of acid. Indian J. Chem. Tech., 18: 291-300.

Smith, C.A., (1984). Stainless steel in the food processing industry. Anti-Corrosion Methods and Materials, 31(4):7-9.

Smith, G.T., Machine tool metrology an industrial Handbook, Southampton Solent University Hampshire, England, Springer.

Taherzadeh, M.J., Karimi, K., (2008). Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: a review. Int. J. Mol. Sci., 9: 1621–51.

Tan, K.W., Kassim, M.J., Oo C.W., (2012). Possible improvement of catechin as corrosion inhibitor in acidic medium. Corros. Sci., 65: 152–162.

Tanaka, A., Zhu, Q., Tan H., Horiba H., Ohnuki K., Mori Y., Yamauchi R., Ishikawa H., Iwamoto A., Kawahara H., ShimizuK., (2014). Biological activities and phytochemical profiles of extracts from different parts of bamboo (phyllostachyspubescens). Molecules, 19: 8238-8260.

Terekhova, E.N., Baklanova, O.N., Lavrenov, A.V., (2017). Carbon containing catalysts for the hydroprocessing of oil fractions: A Review. Catalysis in Industry, 9(2): 110–121.

Tezeghdenti, M., Dhouibi, L., Etteyeb, N., (2015). Corrosion inhibition of carbon steel in 1 M sulphuric acid solution by extract of eucalyptus globulus leaves cultivated in Tunisia arid zones. Journal of Bio-and Tribo-Corrosion, 1(3):16.

Thouri, A., Chahdoura H., El-Arem, A., Hichri, A. O., Hassin, R.B., Achour, L., (2017). Effect of solvents extraction on phytochemical components and biological activities of Tunisian date seeds (var. Korkobbi and Arechti). BMC Complementary and Alternative Medicine, 17: 248.

Tobias, S. A. (ed.), (1980). Proceedings of the twentieth international machine tool design and research conference. Department of Mechanical Engineering. University of Birmingham, UK.

Tokusoglu, O., Unal, M.K., Yemis., (2005). Determination of the phytoalexin resveratrol (3, 5, 4-trihydroxystilbene) in peanuts and pistachios by high performance liquid chromatographic diode array (HPLC-DAD) and gas chromatography-mass spectrometry (GC-MS). J. Agric. Food Chem., 53: 5003-5009.

Trabanelli, G., (1991). Inhibitors an old remedy for a new challenge. Corrosion, 47: 410-419.

Turkmen, N., Sari, F., Velioglu, Y.S., (2006). Effects of extraction solvents on concentration and antioxidant activity of black and black mate tea polyphenols determined by ferrous tartrate and Foline Ciocalteu methods. Food Chem., 99: 835-841.

Umoren S.A., Obot I.B., Israel A.U., Asuquo P.O., Solomon M.M., Eduok U.M., Udoh A.P., (2014). Inhibition of mild steel corrosion in acidic medium using coconut coir dust extracted from water and methanol as solvents. J. Indus. Eng. Chem., 20: 3612–3622.

Umoren S.A., Gasem Z.M., Obot I.B., (2013). Natural products for material protection: inhibition of mild steel corrosion by date palm seed extracts in acidic media. Indus. Eng. Chem. Res., 52(42): 14855-14865.

Umoren S. A., Solomon M. M., Eduok U. M., Obot I. B., Israel A. U., (2014). J. Envir. Chem. Eng., 2(2): 1048-1060.

Valdez, B., Schorr, M., (2004). Stainless steels for corrosion control in the food processing industry. Stainless Steel World 2004. KCI Publishing BV. USA. 419-422.

Vaskova, M., Kotesa, P., Brodnan, M., (2015). Air pollution as an important factor in construction materials deterioration in Slovak Republic. Procedia Engineering. 108: 131 – 138.

Venkatachalam, M., Sathe, S.K. (2006). Chemical composition of selected edible nut seeds. J. Agric. Food. Chem., 54: 4705-4714.

Venzlaff, H., Enning, D., Srinivasan, J., Mayrhofer, K.J.J., Hassel, A.W., Widdel, F., Stratmann M., (2013). Accelerated cathodic reaction in microbial corrosion of iron due to direct electron uptake by sulfate-reducing bacteria. Corros. Sci., 66: 88–96.

Wanklyn, J., (1982). Corrosion monitoring in the oil. Petrochemical and process industries. Oyez Scientific and Technical Services. Lincoln. United Kingdom.

Waseda, Y., Suzuki, S., Ed., (2006). Characterization of corrosion products on steel surfaces, Springer, Berlin.

Wei, N., Jiang, Y., Ying, Y., Guo, X., Wu, Y., Wen, Y., Yang H., (2017). Facile construction of a polydopamine-based hydrophobic surface for protection of metals against corrosion. RSC Adv., 7: 11528 -11536

Weidinger, C., Fischler, F., Schmidpeter, R., Sustainable Entrepreneurship Business Success through Sustainability, ISBN 978-3-642-38752-4, Springer, Heidelberg, New York.

Werner, P., Mehmet, A., (2001). Constitution and magnetism of iron and its alloys. Springer-Verlag. Berlin Heidelberg.

West, J., (1986). Basic corrosion and oxidation. Ellis Horwood Limited. Chichester.

Wright, I.G., (1987). High temperature corrosion. In: Corrosion. ASM Handbook. ASM International., 13: 97–103.

Xu, B., Ji Y., Zhang X., Jin, X., Yang, W., Chen Y., (2015). Experimental and theoretical studies on the corrosion inhibition performance of 4-amino-N, N-di-(2-pyridylmethyl)-aniline on mild steel in hydrochloric acid. RSC Adv., 5: 56049-56059.

Wilbertz, J., (2013). Evaluating societal relevance of research. www.rug.nl/research/ portal/files / 14412466/ evaluating societal relevance.pdf.

Yadav, D.K., Chauhan, D.S., Ahamad, I., Quraishi, M.A., (2013). Electrochemical behavior of steel/acid interface: adsorption and inhibition effect of oligomeric aniline. RSC Adv., 3: 632-646.

Yadav, D.K., Quraishi, M.A. (2012). Application of some condensed uracils as corrosion inhibitors for mild steel: Gravimetric, electrochemical, surface morphological, UV–visible and theoretical investigations. Ind. Eng. Chem. Res., 51(46): 14966–14979.

Yadav, D.K., Quraishi, M.A., Maiti, B., (2012). Inhibition effect of some benzylidenes on mild steel in 1M HCl: An experimental and theoretical correlation. Corros. Sci., 55: 254-266.

Yadav, M., Sarkar, T.K., Obo, I.B., (2016). Carbohydrate compounds as green corrosion inhibitors: electrochemical, XPS, DFT and molecular dynamics simulation studies. RSC Adv., 6: 110053-110069.

Yadav, M., Sinha, R.R., Kumar, S., Sarkar, T.K., (2015). Corrosion inhibition effect of spiropyrimidinethiones on mild steel in 15% HCl solution: insight from electrochemical and quantum studies. RSC Adv.,5: 70832-70848.

Yomgam, Y., Sharma, R., Arya, O.P., Yomgam, Y., (2017). Phytochemical screening and antifungal activities of three medicinal plants from Arunachal Pradesh, India, Journal of Medicinal Plants Studies. 5(3): 278-283.

Yousefi, A., Javadian, S., Dalir, N., Kakemam, J., Akbari, J., (2015). Imidazolium-based ionic liquids as modulators of corrosion inhibition of SDS on mild steel in hydrochloric acid solutions: experimental and theoretical studies. RSC Adv., 5: 11697-11713.

Yuan, Bi-Feng., (2014). Chapter four- 5-methylcytosine and its derivatives. Advances in Clinical Chemistry. 67: 151-187.

Zaabar, A., Aitout, R.., Makhloufi, L. ,Belhamel, K. , Saidani, B., (2014).Inhibition of acid corrosion of mild steel by aqueous nettle extracts. Pigment and Resin Technology, 43(3): 127-138.

Zhang, X., Zheng, Y., Wang, X., Yan, Y., Wu, W., (2014). Corrosion inhibition of N80 steel using novel diquaternary ammonium salts in 15% hydrochloric acid. Ind. Eng. Chem. Res., 53 (37): 14199–14207.

Zhao, J., Chen G., (2012). The synergistic inhibition effect of oleic-based imidazoline and sodium benzoate on mild steel corrosion in a $CO_2$-saturated brine solution. Electrochimica Acta, 69: 247– 255.

Zheng, H., Lui K., Nee A. (ed.), (2013). Machinability of Engineering Materials, Springer London.

Zheng, X., Gong, M., Li, Q., Guo, L.,(2018). Corrosion inhibition of mild steel in sulfuric acid solution by loquat (Eriobotrya japonica Lindl.) leaves extract, Scientific Reports, 8:9140.

Zhou, L., Li H., Shi, C., (2008). Materials research in China, Nature Mater., 7: 603 - 605.

Zhou, Y., Guo, Li, Zhang, S., Kaya, S., Luoa X., Xiang B., (2017). Corrosion control of mild steel in 0.1 M $H_2SO_4$ solution by benzimidazole and its derivatives: an experimental and theoretical study. RSC Adv., 7: 23961–23969.

# LIST OF PUBLICATIONS

A. Journals

International Journals

1. JP Rajan, KB Singh, S Kumar, RK Mishra. (2014). Trace elements content in the selected medicinal plants traditionally used for curing skin diseases by the natives of Mizoram, India. Asian Pacific journal of tropical medicine. 7. S410-S414.

2. JP Rajan, R Shrivastava, RK Mishra. (2017). Corrosion inhibition effect of Clerodendron colebrookianum walp leaves (phuinam) extract on the acid corrosion of mild steel. Protection of Metals and Physical Chemistry of Surface.53. 6: 1161-1172.

National Journals

1. Ruchi Shrivastava, Jay Prakash Rajan and Raj Kumar Mishra. (2016). Melocanna baccifera (Bamboo) Leaves as Corrosion Inhibitors for Iron in Acidic Media. Science and Technology Journal. 4: 56-59.

2. J P Rajan, R. K. Mishra and K.B. Singh. (2019). Element and Phytochemicals profile in ethno medicinal plants used for treating cardiovascular diseases by Mizo-tribe of north eastern India. Asian journal of chemistry. 31(6):1237-1242.

Book chapters

1. Jay Prakash Rajan, RK Mishra, Study of Methanolic extract of Spilanthes acmella as corrosion inhibitor of mild steel in 1 N HCl and 1 N H2SO4. MatCon 2016 ISBN: 978-93-80095-738.

2. Jay Prakash Rajan, RK Mishra. Study of the methanolic extract of flower of wild sunflower (Tithonia diversifolia) as corrosion inhibitors of mild steel in acidic medium.

Chapter10.Natural product chemistry. Editor Niranjan Das, Write and Print Publication, New Delhi. 2017, 144-149. ISBN: 978-93-86283-54-2.

B. Paper presented in Conferences / Symposia

Conferences and Seminars attended and presented

1. Paper entitled “Study of the value addition by product from biodiesel via trans-esterification of vegetable oil; National Seminar on Economic Development in North East India: Challenges and opportunities” presented in National Seminar on Economic Development in North East India: Challenges and opportunities organized by Department of Commerce and Department of Economics, Pachhunga University College, Aizawl, Mizoram; 2013

2. Paper entitled “Study of methanolic extract of flower of wild sunflower (Tithonia diversifolia) as corrosion inhibitors of mild steel in Acidic medium” presented in National Seminar on Recent Advances in Natural Products Chemistry for Drug Discovery organized by Netaji Subhas Mahavidyalaya, Udaipur, Gomati, Tripura;2015

7. Paper entitled “Study of methanolic extract of Spilanthes acmella as corrosion inhibitor of mild steel in 1 N HCl and 1N $H_2SO_4$ Acidic Medium” presented in International Conference on Materials for the Millennium organized by Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, Kerla; 2016

8. Paper entitled “Evaluation of Allium hookeri methanolic plant extract as a potential ecofriendly corrosion inhibitor of mild steel in 1N HCl acidic medium” presented in International Conference on Thermal, Energy and Environment organized by Department of Mechanical Engineering, Kalasalingam University, Anand Nager, Krishnankoil, Tamilnadu; 2016

Workshop

1. Participated (December 15-20th 2014) in the workshop on Electron Microscopy (FE-SEM with EDAX & TEM) organized by SICART, Vallabh Vidyanagar, Gujarat.

2. Participated (February 16-20th 2015) in the state level workshop on C++ language and numerical method, organized by department of physics and mathematics, Pachhunga University College, Aizawl-796001, Mizoram.

## Particulars of the candidate

Name of candidate : Jay Prakash Rajan

Degree : Ph.D

Department : Chemistry

Title of thesis : Studies of plant extracts as eco-friendly corrosion inhibitors

Date of admission : 3rd august 2012

Approval of research proposal :

1. B.O.S. : 30th April 2013

2. SCHOOL BOARD REGISTRATION NO. & DATE :MZU/Ph.D/ 558 of 20.05.2013

Extension (if any) : Nil

(Prof. Diwakar Tiwari)
Head

Head
Chemistry Department
Mizoram University
Mizoram : Aizawl

# Bio-Data

| | |
|---|---|
| Name | Jay Prakash Rajan |
| Designation | Assistant Professor |
| Department | Chemistry |
| Address (r) | House no. 19/B, Kulikawn<br>Aizawl |
| Phone no | 8415851604 |
| Email | Jaypr33@gmail.com |
| Date of Birth | 05/01/1976 |

Education

| Degree | Institution | Year | Details |
|---|---|---|---|
| B.Sc. | Ranchi University | 2001 | 2nd (Chemistry) |
| M.Sc. | Ranchi University | 2004 | 1st (Chemistry) |
| M.Tech | Cochin University of Science And Technology | 2007 | 1st (Industrial Catalysis) |
| Ph.D | Mizoram University | 2019 | Chemistry |
| Any Other | | | |

Career Profile

| Institution | Designation | Duration | Role |
|---|---|---|---|
| Pachhunga University College (Mizoram University) | Assistant Professor | Since 20th March 2007 | Faculty |

Research interest/ Specialization: Corrosion, Catalysis, Medicinal Plant, Trace metal.

Subjects taught: 1.Organic Chemistry 2. Physical Chemistry
3. Analytical Chemistry 4. Industrial Chemistry

Honours & awards: GATE-2004, CSIR- NET -2005

## Publication

| Year | Title | Publisher/ journal |
|---|---|---|
| 2014 | Trace elements content in the selected medicinal plants traditionally used for curing skin diseases by the natives of Mizoram, India. | Asian Pacific journal of tropical medicine, 7(2014), S410-S414 |
| 2016 | Melocanna baccifera (Bamboo) Leaves as Corrosion Inhibitors for Iron in Acidic Media. | Science & Technology Journal. 4(2016). 56-59 |
| 2017 | Corrosion inhibition effect of Clerodendron colebrookianum walp leaves (phuinam) extract on the acid corrosion of mild steel. | Protection of Metals and Physical Chemistry of Surfaces |
| 2019 | Element and Phytochemicals profile in ethno medicinal plants used for treating cardiovascular diseases by Mizo-tribe of north eastern India. | Asian journal of chemistry. 31(6):1237-1242. |
| 2016 | Study of Methanolic extract of Spilanthes acmella as corrosion inhibitor of mild steel in 1 N HCl and 1 N $H_2SO_4$. | MatCon 2016 ISBN: 978-93-80095-738 |
| 2017 | Study of the methanolic extract of flower of wild sunflower (Tithonia diversifolia as corrosion inhibitors of mild steel in acidic medium. | Chapter 10. Natural product chemistry. Editor Niranjan Das, Write and Print Publication, New Delhi. 2017, 144-149. ISBN: 978-93-86283-54-2. |

## Conference /Seminar/Workshop attended

| Year | Name of the conference/seminar | Organizer |
|---|---|---|
| 2013 | Paper presented entitled “Study of the value addition by | Department of |

| | | |
|---|---|---|
| | product from biodiesel via transeferication of vegetable oil; National Seminar on Economic Development in North East India : Challenges and opportunities" National Seminar on Economic Development in North East India : Challenges and opportunities. | Commerce and Department of Economics, Pachhunga University College, Aizawl, Mizoram; 2013 |
| 2015 | Paper presented entitled "Study of methanolic extract of flower of wild sunflower (Tithonia diversifolia) as corrosion inhibitors of mild steel in Acidic medium" National Seminar on Recent Advances in Natural Products Chemistry for Drug Discovery. | Netaji Subhas Mahavidyalaya, Udaipur, Gomati, Tripura;2015 |
| 2016 | Paper presented entitled "Study of methanolic extract of Spilanthes acmella as corrosion inhibitor of mild steel in 1 N HCl and 1N $H_2SO_4$ Acidic Medium" International Conference on Materials for the Millennium. | Department of Applied Chemistry, Cochin University of Science & Tech., Kochi, Kerla |
| 2016 | Paper presented entitled "Evaluation of Allium hookeri methanolic plant extract as a potential eco friendly corrosion inhibitor of mild steel in 1N HCl acidic medium" presented in International Conference on Thermal, Energy and Environment . | Department of Mech. Eng., Kalasalingam University , Anand Nager, Krishnankoil, Tamilnadu; 2016 |
| 2018 | Paper presented entitled "Enhancement of Bamboo utilization by chemical treatment" | Dept. of Geography, Pachhunga University College, Aizawl, Mizoram. |

## Projects & Collaborations

UGC Minor Research Project completed Entitled " Evaluation of trace minerals (Zn, Cu, Mn, Fe, Cr, Mn and Se) concentration in selected ethno-medicinal plant of Mizoram"