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24-06-2022

CERTIFICATE

*I hereby certify that, this is the revised version of the thesis entitled "**Synthetic and natural organic inhibitors for metal corrosion: physicochemical, electrochemical, morphological and quantum mechanical investigations**" submitted by **Ms. Vidhya Thomas K** under my guidance after incorporating the necessary corrections/suggestions made by the adjudicators. Also certify that the contents in the thesis and the soft copy are one and the same.*

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CERTIFICATE

This is to certify that the thesis entitled ***"Synthetic and natural organic inhibitors for metal corrosion: physicochemical, electrochemical, morphological and quantum mechanical investigations****" is an authentic record of research work carried out by* ***Ms. VIDHYA THOMAS K*** *under my supervision in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in Chemistry of University of Calicut and further that no part thereof has been presented before for any other degree.*

Dr. Joby Thomas. K

(Supervising Teacher)

DECLARATION

I hereby declare that the thesis entitled, “Synthetic and natural organic inhibitors for metal corrosion: physicochemical, electrochemical, morphological and quantum mechanical investigations”, submitted to the University of Calicut in partial fulfillment of the requirements for the award of the Degree of Doctor of Philosophy in Chemistry is a bonafide research work done by me under the supervision and guidance of Dr. Joby Thomas. K, Former Associate Professor & Former Head, Department of Chemistry, St. Thomas’ College (Autonomous), Thrissur, Kerala.

I further declare that this thesis has not previously formed the basis of any degree, diploma or any other similar title.

2-11-2021 VIDHYA THOMAS K

To

My Family

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Vidhya Thomas K

ABBREVIATIONS

ICE	*Ixora coccinea* extract
CPE	*Croton persimilis* extract
TCE	*Tinospora cordifolia* extract
GCE	*Garcinia cambogia* extract
CILE	*Clerodendrum infortunatum* leaf extract
CIRE	*Clerodendrum infortunatum* root extract
DBE	*Dioscorea bulbifera* extract
HCA	Hydroxy citric acid
NHP2M	N-hydroxy-1-(pyridin-2-yl)methanimine
NHP3M	N-hydroxy-1-(pyridin-3-yl)methanimine
2PHEP	(E)-2-(1-(2-phenylhydrazono) ethyl)pyridine
2TAEP	(E)-2-(1-triazylidineethyl)pyridine
SCC	Stress corrosion cracking
HIC	Hydrogen-induced cracking
EIC	Environmentally induced cracking
CFC	Corrosion-fatigue cracking
GDP	Gross domestic product
VPIs	Vapour phase inhibitors
DMSO	Dimethyl sulphoxide
EIS	Electrochemical impedance spectroscopy
FTIR	Fourier-transform infrared
UV-Vis	Ultraviolet-visible
NMR	Nuclear magnetic resonance
LC-MS	Liquid chromatography-mass spectrometry
SCE	Saturated calomel electrode
OCP	Open circuit potential
ECN	Electrochemical noise

PSD	Power spectral density
FFT	Fast Fourier transform
MEM	Maximum entropy method
MM	Molecular mechanics
DFT	Density functional theory
SE	Semi-empirical
STO	Slater type orbitals
SEM	Scanning electron microscopy
AFM	Atomic force microscopy
MO	Molecular orbital
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
RSM	Response surface methodology
CCD	Central Composite Design
ANOVA	Analysis of variance
BBD	Box-Behnken Design
MIC	Microbial induced corrosion
EPS	Extracellular polymeric substances
SRB	Sulphate reducing bacteria
SOB	Sulphur oxidizing bacteria
IB	Iron oxidizing/depositing bacteria
MnB	Manganese oxidizing/depositing bacteria
APB	Acid-producing bacteria
MHA	Mueller-Hinton agar
PCR	Polymerase Chain Reaction
XRD	X-ray diffraction spectroscopy
TEM	Transmission electron microscopy
IE	Inhibition efficiency

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CHAPTER 5

PREFACE

In recent years, the regulation of metal corrosion had a great interest in the field of scientific research. Ready availability, notable mechanical strength and affordable cost make mild steel a widely used alloy in industrial applications. However, the deterioration of mild steel remains a critical issue for the community by considering safety and economic matters. Acid media is used to clean boilers and massive equipment made from mild steel in large scale production units. But it causes metal corrosion. Mitigation of metal corrosion during acid treatment requires appropriate acid solutions. High-cost synthesis and hazardous influence on the atmosphere and human beings make synthetic inhibitors unfriendly inhibitors. The application of extracts from natural products like leaves, fruits, stems, seeds and roots as green corrosion inhibitors can overcome the limitations of the synthetic inhibitors. Plant products can adsorb the surface of the metal either by physical or chemical adsorption. This shielding behaviour of the natural products on the metal surface is due to numerous phytochemicals, which can interact with the metal surface by donating lone pair of electrons of heteroatoms, unsaturated and aromatic systems. Thus, the employment of eco-friendly corrosion inhibitors has a significant role in chemical research.

Microbial induced corrosion (MIC) is the destruction of a metal by the activity of living organisms either directly by enhancing the electrochemical reactions or indirectly because of their metabolic products. Various environments such as soil, natural waters, seawater, natural petroleum products and oil emulsion cutting fluids encounter corrosion by such biological activity. MIC is termed for corrosion by the occupancy and activities of microbes within biofilms at metal surfaces. Biocides are a standard chemical method applied as a MIC mitigation solution. Plant extracts are considered natural sources of antimicrobial agents. Schiff bases accounted for their high inhibition efficiency among

various synthetic organic inhibitors due to their electronic and structural properties. They can coordinate with the metal surface through π-electrons from double bonds and lone pairs of electrons from nitrogen.

The present work is an effort to find out potentially active natural corrosion inhibitors for mild steel in acid media and apply Schiff base inhibitors for MIC in marine environments. Some of the medicinal plants primarily available in our countryside are investigated as natural inhibitors for acid corrosion.

This thesis is divided into nine chapters.

CHAPTER 1: Introduction and Review

This chapter encompasses the introductory session and thorough review of this thesis. It provides an idea about the social and economic aspects of corrosion, types of corrosion, corrosion chemistry, and the need and methods for corrosion control. An introduction to MIC, causes of MIC and strategies to reduce MIC are also discussed in this chapter. The different experimental and quantum mechanical calculations adopted in the investigation for monitoring corrosion and the theories behind all these methods are included here. This chapter reviews natural and synthetic compounds as acid corrosion inhibitors and MIC corrosion inhibitors, respectively. This chapter is concluded by giving the scope and aim of the present investigations.

CHAPTER 2: Materials and Methods

This chapter deals with the experimental details regarding the whole work. The preparation of the extracts, materials and medium for acid corrosion are described here. The technical details of various corrosion monitoring studies, the operational aspects of quantum mechanical studies and statistical analysis methods are explained in this session. It also contains methods and reagents used for preparing medium for MIC inhibition studies, isolation and identification of bacterium from original seawater and

MIC corrosion monitoring techniques.

CHAPTER 3: *Ixora coccinea* Extract: Natural Corrosion Inhibitor for Mild Steel in Acid Media

This chapter discusses the corrosion inhibition behaviour of *Ixora coccinea* leaf extract (ICE). Phytochemical screening, FTIR spectroscopy, Weightloss measurements, Electrochemical impedance spectroscopy (EIS), Potentiodynamic polarization, Electrochemical noise measurements, adsorption, UV-Visible spectroscopy, temperature studies and surface morphological studies were carried out. Theoretical calculations of the major component ixorene have been performed. Statistical analysis of factors has also been studied using Response surface methodology and Central composite design. It was proved that ICE act as a good inhibitor for mild steel corrosion in 1 M HCl and 0.5 M H_2SO_4.

CHAPTER 4: *Croton persimilis* Extract: Natural Corrosion Inhibitor for Mild Steel in Acid Media

This chapter encompasses the study of the anti-corrosion behaviour of *Croton persimilis* leaf extract (CPE). The ethanolic extract of CPE was investigated as inhibitor for mild steel in 1 M HCl and 0.5 M H_2SO_4 media at room temperature. Electrochemical studies revealed the excellent inhibition capacity of CPE in 0.5 M H_2SO_4 than 1 M HCl, which was supported by adsorption studies, temperature and surface morphological studies. Theoretical calculations of the significant components neocrotocembraneic acid and stigmasterol have been performed. Statistical analysis of factors has also been studied using Response surface methodology and Central composite design.

CHAPTER 5: *Tinospora cordifolia* Extract: Natural Corrosion Inhibitor for Mild Steel in Acid Media

The inhibiting capacity of *Tinospora cordifolia* extract (TCE) has been evaluated on mild steel in 1M HCl and 0.5 M H_2SO_4 by physicochemical and electrochemical techniques and by utilizing statistical tools such as response surface methodology (RSM)

and Box-Behnken design (BBD) in this chapter. Surface properties have been ascertained by atomic force microscopy (AFM) to confirm the adsorption performance of the inhibitor molecules on the surface of the metal. Experimental results were found to agree with quantum chemical calculations of the active principle of TCE, Tinosponone.

CHAPTER 6: *Garcinia cambogia* Extract: Natural Corrosion Inhibitor for Mild Steel in Acid Media

This chapter illustrates the corrosion-resistant power of the ethanol extract of *Garcinia cambogia* (GCE) leaves for mild steel in 1 M HCl and 0.5 M H_2SO_4. Gravimetric, electrochemical and morphological studies have been established to authenticate inhibiting power of GCE. Quantum mechanical investigations of chief constituents, hydroxycitric acid and hydroxycitric acid lactone have been shown the anticorrosion behaviour of GCE. Statistical analysis using response surface methodology and Box-Behnken design was proved a good agreement with experimental results.

CHAPTER 7: *Clerodendrum infortunatum* Extract: Natural Corrosion Inhibitor for Mild Steel in Acid Media

This chapter deals with physicochemical, electrochemical and surface morphological studies of the inhibitive interaction of *Clerodendrum infortunatum* leaf and root extracts (CILE and CIRE) on the mild steel surface in 1 M HCl and 0.5 M H_2SO_4. The extracts showed appreciable efficiencies in varying inhibitor concentrations. The major components clerodin and scutellarin have also been analyzed for their inhibitory action. Predicted inhibition efficiency of CIRE at different CIRE concentrations and operating temperature in 1 M HCl evaluated by RSM was in perfect agreement with the data obtained from weight loss measurements.

CHAPTER 8: *Dioscorea bulbifera* Extract: Natural Corrosion Inhibitor for Mild Steel in Acid Media

This chapter explores the potent corrosion inhibition property of green *Dioscorea bulbifera* leaf extract (DBE) on the mild steel in 1 M HCl and 0.5 M H_2SO_4 using

physicochemical, electrochemical and surface morphological techniques. Three essential chemical components, bafoudiosbulbin A, diosgenin and kaempferol, have been subjected to quantum mechanical studies to supplement the corrosion inhibition mechanism of the leaf extract in more detail. By designing BBD, response surface methodology has been applied to validate the interdependence between DBE concentration, HCl concentration, and temperature on the inhibition efficiency. DBE was found to be an efficient corrosion inhibitor for mild steel corrosion exposed in 1 M HCl and 0.5 M H_2SO_4.

CHAPTER 9: Schiff Bases Derived from Pyridine Carbonyl Compounds: Synthetic Microbial Induced Corrosion Inhibitor for Mild Steel in Marine Environment

This chapter deals with microbial induced corrosion (MIC) behaviour of four synthetic inhibitors derived from pyridine carbaldehyde and acetyl pyridine on mild steel in the artificial seawater medium, 1) *N*-hydroxy-1-(pyridin-2-yl)methanimine, NHP2M 2) *N*-hydroxy-1-(pyridin-3-yl)methanimine, NHP3M 3) (E)-2-(1-(2-phenylhydrazono) ethyl)pyridine, 2PHEP and 4) (E)-2-(1-triazylidineethyl)pyridine, 2TAEP. It includes isolation and identification of bacterium from original seawater and corrosion monitoring methods like physicochemical and electrochemical techniques of these Schiff bases. Mechanism of corrosion was established by *in vitro* antibacterial effects of Schiff bases, surface analysis, microscopic surface analysis and UV-Vis spectroscopy.

An overall summary of these investigations is also reported at the end of this part, followed by the bibliography.

LIST OF PUBLICATIONS

- **Vidhya Thomas K**, Joby Thomas K, Vinod Rapheal P, A.S. Sabu, K. Ragi, Reeja Johnson. "*Tinospora cordifolia* extract as an environmentally benign green corrosion inhibitor in acid media: electrochemical, surface morphological, quantum chemical, and statistical investigations", *Materials Today Sustainability*, vol.13, 100076 (2021) https://doi.org/10.1016/j.mtsust.2021.100076

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- **Vidhya Thomas K**, Joby Thomas K, Ragi K, Reeja Johnson."Excellent eco-friendly corrosion inhibition behaviour of *Croton persimilis* extract (CPE) for mild steel in acidic media: physicochemical, electrochemical and surface morphological studies", *National seminar on Current Trends in Chemistry (CTriC 2020),* CUSAT, February 2020

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- Shaju K S, Joby Thomas K, **Vidhya Thomas K**, Vinod P Rapheal."Synthesis, characterization and redox properties of Schiff base derived from 3-mercapto propanoic acid and its Cu(II) complex", *KSCSTE Sponsored National Seminar on Interdisciplinary Chemical Research*, St Joseph's College(autonomous), Irinjalakuda, February 2018.

- Shaju K S, Joby Thomas K, **Vidhya Thomas K**,Vinod P Rapheal. "Cyclic voltammetric studies of Schiff base derived from 3-Phenylpropanoic acid and its Cu(II) complex in DMSO at the surface of glassy carbon", *UGC sponsored National seminar on Recent Advances in Chemistry*, Vimala College,Thrissur,January2017

PAPERS TO BE COMMUNICATED

- Schiff bases derived from pyridine carbonyl compounds as synthetic microbial induced corrosion inhibitor for mild steel in marine environment.

- Influence of leaves and roots extracts of *Clerodendrum infortunatum* as eco-friendly corrosion inhibitor on mild steel in acid media: Experimental and theoretical approach