

**CORROSION INHIBITION PERFORMANCE OF ROSEMARY  
OIL ON CARBON STEEL IN ACID AND SALINE  
ENVIRONMENTS**

OLOMUKORO, OBOROGHENE TOPE

(06CF04147)

NOVEMBER, 2020

**CORROSION INHIBITION PERFORMANCE OF ROSEMARY  
OIL ON CARBON STEEL IN ACID AND SALINE  
ENVIRONMENTS**

**OLOMUKORO, OBOROGHENE TOPE**

**(06CF04147)**

**B.Eng. (Hons) Chemical Engineering, Covenant University, Ota**

**A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE  
STUDIES IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE  
AWARD OF THE MASTER OF ENGINEERING DEGREE IN CHEMICAL  
ENGINEERING IN THE DEPARTMENT OF CHEMICAL ENGINEERING,  
COLLEGE OF ENGINEERING, COVENANT UNIVERSITY.**

**NOVEMBER, 2020**

## ACCEPTANCE

This is to attest that this dissertation is accepted in partial fulfilment of the requirements for the award of the degree of Master of Engineering (M.Eng) in Chemical Engineering in the Department of Chemical Engineering, College of Engineering, Covenant University, Ota, Nigeria.

**Mr. John A. Philip**

(Secretary, School of Postgraduate Studies)

Signature and Date

**Prof. Akan B. Williams**

(Dean, School of Postgraduate Studies)

Signature and Date

## **DECLARATION**

I, **OLOMUKORO, OBOROGHENE TOPE (06CF04147)** declares that this research was carried out by me under the supervision of Dr. O. A. Odunlami of the Department of Chemical Engineering, College of Engineering, Covenant University, Ota, Nigeria. I attest that the dissertation has not been presented either wholly or partially for the award of any degree elsewhere. All sources of data and scholarly information used in this dissertation are duly acknowledged.

**OLOMUKORO, OBOROGHENE TOPE**

**Signature and Date**

## CERTIFICATION

We certify that this dissertation titled “**THE CORROSION INHIBITION PERFORMANCE OF ROSEMARY OIL ON CARBON STEEL IN ACIDIC AND SALINE ENVIRONMENTS**” is an original research work carried out by **OLOMUKORO, OBOROGHENE TOPE (06CF04147)** in the Department of Chemical Engineering, College of Engineering, Covenant University, Ota, Ogun State, Nigeria under the supervision of Dr. Olayemi A. Odunlami. We have examined and found this work acceptable as part of the requirements for the award of the degree of Master of Engineering (M. Eng) in Chemical Engineering.

**Dr. Olayemi A. Odunlami**

(Supervisor)

Signature and Date

**Dr. Augustine O. Ayeni**

(Head of Department)

Signature and Date

**Prof. Oladipupo O. Ogunleye**

(External Examiner)

Signature and Date

**Prof. Akan B. Williams**

(Dean, School of Postgraduate Studies)

Signature and Date

## **DEDICATION**

*“But there is a spirit in man: and the inspiration of the Almighty giveth them understanding”*  
- Job 32:8 (KJV)

This research work is dedicated to almighty God for wisdom, knowledge and understanding. Also to my ever loving, caring and dependable parents: Prof. & Prof. (Mrs) J. O Olomukoro for their immense support.

## ACKNOWLEDGEMENTS

I appreciate God for life, strength and health, without which, this research work would have been far from completion. To Him alone be the Glory.

To my wonderful parents, Prof. & Prof. (Mrs) J. O. Olomukoro for their immense support spiritually and financially. I cannot thank them enough. They will surely reap their investments.

The Chancellor of Covenant University, Dr. David Oyedepo: a spiritual father and revolutionary leader whom God has empowered in creating a conducive environment for learning and research. The Lord continue to empower you for greater exploits. The entire management of Covenant University, particularly the Vice Chancellor, Prof. A.A.A Atayero and the Dean, School of Postgraduate Studies, Prof. Abiodun H. Adebayo for their tireless efforts in ensuring a research-driven institution.

The Head of Department, Chemical Engineering, Dr. A.O. Ayeni. I appreciate your interest in the progress of my work. My deep appreciation goes to my Supervisor, Dr. O. A. Odunlami for her efforts, patience, support and words of advice in ensuring a thorough work was carried out. My experimental work would not have been possible without the generosity of Prof. R.T. Loto of the Department of Mechanical Engineering for allowing me conduct my experiments in his laboratory. I also appreciate Engr. Muyiwa Fajobi, a Ph.D student of the Department of Mechanical Engineering for his assistance in the experimental set-up and provision of useful materials for my write-up. I will not forget Engr. Adegbite, lab technologist of the Department of Chemical Engineering for his help in the preparation of my solutions.

Lastly, I appreciate my fellow postgraduate colleagues: Godswill Ekanem, Deinma Dick, Isaac Ekere, Akinleye Sowunmi, Esther Afolabi, Omololu Fagbiele, Daniel Oyekunle, Tomiwa Oguntade among others for their show of concern in the progress of my work.

May God Almighty perfect all issues of concern in the life of everyone that made this research work a success. Amen.

## TABLE OF CONTENTS

<b>CONTENT</b>	<b>PAGE</b>
<b>COVER PAGE</b>	i
<b>TITLE PAGE</b>	ii
<b>ACCEPTANCE</b>	iii
<b>DECLARATION</b>	iv
<b>CERTIFICATION</b>	v
<b>DEDICATION</b>	vi
<b>ACKNOWLEDGEMENTS</b>	vii
<b>TABLE OF CONTENTS</b>	viii
<b>LIST OF FIGURES</b>	xii
<b>LIST OF TABLES</b>	xiv
<b>LIST OF PLATES</b>	xvi
<b>ABSTRACT</b>	xvii
 <b>CHAPTER ONE: INTRODUCTION</b>	
1.1 Background of the Study	1
1.2 Statement of the Research Problem	3
1.3 Aim and Objectives of Study	4
1.4 Scope of Research	4
1.5 Justification of Study	4
 <b>CHAPTER TWO: LITERATURE REVIEW</b>	
2.1 Rosemary Plant	5
2.1.1 History and applications	5
2.1.2 Phytochemical constituents and essential oils of rosemary plant	6
2.1.3 Properties of rosemary oil	9
2.2 Carbon Steels	11
2.2.1 Corrosion in carbon steels	11
2.3 Corrosion Inhibitors	12



2.3.1	Mechanism of inhibitors	13
2.3.2	Classification of inhibitors	13
2.3.3	Green inhibitors	14
2.4	Adsorption Isotherm	20
2.5	Corrosion Theory and Mechanism	22
2.6	Corrosion Kinetics and Thermodynamics	22
2.7	Electrochemistry of Corrosion	24
2.8	Corrosion in Different Environments	26
2.8.1	Natural environments	27
2.8.2	Organic environment	30
2.8.3	Organic acids	30
2.9	Activity of Metals in Corrosive Environments	31
2.10	Forms of Corrosion	32
2.10.1	Uniform corrosion	32
2.10.1.1	Atmospheric corrosion	33
2.10.1.2	Galvanic corrosion	33
2.10.2	Localised corrosion	34
2.10.2.1	Pitting corrosion	35
2.10.2.2	Crevice corrosion	37
2.10.2.3	Intergranular corrosion	37
2.10.3	Metallurgically influenced corrosion	38
2.10.3.1	Dealloying corrosion	38
2.10.4	Mechanically assisted degradation	39
2.10.4.1	Erosion corrosion	39
2.10.4.2	Fretting corrosion	39
2.10.4.3	Cavitation corrosion	39
2.10.5	Environmentally induced cracking corrosion	40
2.10.5.1	Stress corrosion cracking	40
2.10.5.2	Hydrogen damage	41

2.11	Corrosion Testing and Monitoring Techniques	42
2.11.1	Corrosion monitoring	42
2.11.1.1	Importance of corrosion monitoring	42
2.11.2	Corrosion monitoring techniques	42

### **CHAPTER THREE: MATERIALS AND METHODS**

3.1	Materials	44
3.1.1	High carbon steel	44
3.1.2	Rosemary oil	44
3.1.3	Chemicals used	45
3.1.4	Apparatus used	45
3.2	Preparation of Solutions	46
3.2.1	Citric acid preparation	46
3.2.2	Sulphuric acid preparation	46
3.2.3	Sodium chloride preparation	47
3.3	Weight Loss Experiment Procedures	47
3.4	Potentiodynamic Polarization Procedures	48
3.5	Adsorption Isotherms	49
3.6	Thermodynamics of Corrosion Inhibition Mechanism	50

### **CHAPTER FOUR: RESULTS**

4.1	Weight Loss	52
4.1.1	Weight loss of carbon steel in citric acid solution	52
4.1.2	Weight loss of carbon steel in sulphuric acid solution	53
4.1.3	Weight loss of carbon steel in sodium chloride solution	54
4.2	Corrosion Rate	55
4.2.1	Corrosion rate of carbon steel in citric acid solution	55
4.2.2	Corrosion rate of carbon steel in sulphuric acid solution	56
4.2.3	Corrosion rate of carbon steel in sodium chloride solution	57

4.3	Inhibition Efficiency	58
4.3.1	Inhibition efficiency of rosemary oil in citric acid solution	58
4.3.2	Inhibition efficiency of rosemary oil in sulphuric acid solution	59
4.3.3	Inhibition efficiency of rosemary oil in sodium chloride solution	60
4.4	Potentiodynamic Polarization Plots	61
4.5	Adsorption Isotherms	62
4.5.1	Langmuir isotherm for sulphuric acid solution	62
4.5.2	Langmuir isotherm for citric acid solution	64
4.5.3	Langmuir isotherm for sodium chloride solution	64
4.5.4	Freundlich isotherm for citric acid solution	65
4.5.5	Freundlich isotherm for sulphuric acid solution	66
4.6	Thermodynamics Calculations	67
4.6.1	Thermodynamics calculations for citric acid solution	67
4.6.2	Thermodynamics calculations for sulphuric acid solution	68
4.6.3	Thermodynamics calculations for sodium chloride solution	68
<b>CHAPTER FIVE: DISCUSSION</b>		
5.1	Weight Loss	69
5.2	Corrosion Rate	70
5.3	Inhibition Efficiency	70
5.4	Potentiodynamic Polarization Experiment	71
5.5	Adsorption Isotherm	72
5.6	Thermodynamic Calculations	72
<b>CHAPTER SIX: CONCLUSION AND RECOMMENDATION</b>		
6.1	Conclusion	73
6.2	Contributions to Knowledge	73
6.3	Recommendation	74
<b>REFERENCES</b>		75

## LIST OF FIGURES

<b>Figures</b>	<b>Title of Figures</b>	<b>Page</b>
2.1	The chemical structure of carsonic acid, carnosol and rosmarinic acid	7
2.2	Chemical compounds present in the essential oil of Rosemary plant	9
2.3	Schematic sketch of uniform corrosion	33
2.4	Schematic sketch of galvanic corrosion	34
2.5	Schematic sketch of pitting corrosion mechanism	36
2.6	Schematic sketch of crevice corrosion mechanism	37
2.7	Schematic sketch of intergranular corrosion	38
2.8	Schematic sketch of dealloying corrosion	38
2.9	Schematic sketch showing a combination of erosion, cavitation and fretting corrosion	40
2.10	Schematic sketch of stress corrosion cracking	41
2.11	Hydrogen induced corrosion cracking	42
4.1	Weight loss versus exposure time for carbon steel in citric acid solution	53
4.2	Weight loss versus exposure time for carbon steel in sulphuric acid solution	54
4.3	Weight loss versus exposure time for carbon steel in sodium chloride solution	55
4.4	Corrosion rate versus exposure time for carbon steel in citric acid solution	56
4.5	Corrosion rate versus exposure time for carbon steel in sulphuric acid solution	57
4.6	Corrosion rate versus exposure time for carbon steel in sodium chloride Solution	58
4.7	Inhibition efficiency against exposure time in citric acid solution	59
4.8	Inhibition efficiency against exposure time in sulphuric acid solution	60
4.9	Inhibition efficiency against exposure time in sodium solution chloride	61
4.10	Potentiodynamic polarization plot for carbon steel in citric acid solution	61

4.11	Potentiodynamic polarization plot for carbon steel in sulphuric acid solution	62
4.12	Potentiodynamic polarization plot for carbon steel in sodium chloride solution	62
4.13	Langmuir isotherm plot of $c/\theta$ against $\theta$ in sulphuric acid solution	63
4.14	Langmuir isotherm plot of $c/\theta$ against $\theta$ in citric acid solution	64
4.15	Langmuir isotherm plot of $c/\theta$ against $\theta$ in sodium chloride solution	65
4.16	Freundlich isotherm plot of $\ln \theta$ against $\ln C$ in citric acid solution	65
4.17	Freundlich isotherm plot of $\ln \theta$ against $\ln C$ in sulphuric acid solution	66
4.18	Freundlich isotherm plot of $\ln \theta$ against $\ln C$ in sodium chloride solution	67

## LIST OF TABLES

<b>Table</b>	<b>Title of Tables</b>	<b>Page</b>
2.1	Therapeutic benefits of rosemary plant in different regions	6
2.2	Chemical composition of rosmary essential oil	8
2.3	Chemical and physical properties of rosemary oil and selected terpenes	10
2.4	Concentration of ions and molecules in clean sea water	29
3.1	Percentage composition of high carbon steel	44
4.1	Weight loss measurement data for carbon steel in citric acid solution	52
4.2	Weight loss measurement for carbon steel in sulphuric acid solution	53
4.3	Weight loss measurement data for carbon steel in sodium chloride solution	54
4.4	Corrosion rate data for carbon steel in citric acid solution	55
4.5	Corrosion rate data for carbon steel in sulphuric acid solution	56
4.6	Corrosion rate for carbon steel in sodium chloride solution	57
4.7	Inhibition efficiency data for carbon steel in citric acid solution	58
4.8	Inhibition efficiency data for carbon steel in sulphuric acid solution	59
4.9	Inhibition efficiency data for carbon steel in sodium chloride solution	60
4.10	Langmuir isotherm data for sulphuric acid solution	63
4.11	Langmuir isotherm data for citric acid solution	64
4.12	Langmuir isotherm data for sodium chloride	64
4.13	Freundlich isotherm data for citric acid solution	65
4.14	Freundlich isotherm data for sulphuric acid solution	66
4.15	Freundlich isotherm data for sodium chloride solution	66
4.16	Data obtained for Gibbs free energy, surface coverage and equilibrium constant of adsorption for Rosemary oil adsorption in citric acid solution	67

4.17	Data obtained for Gibbs free energy, surface coverage and equilibrium constant of adsorption for rosemary oil adsorption in sulphuric acid solution	68
4.18	Data obtained for Gibbs free energy, surface coverage and equilibrium constant of adsorption for rosemary oil adsorption in sodium chloride solution	68

## LIST OF PLATES

<b>Plate</b>	<b>Title of Plates</b>	<b>Page</b>
2.1	Rosemary plant	5
3.1	Rosemary essential oil	45
3.2	Electronic weighing balance	45
3.3	Optical microscope	46
3.4	Potentiotat setup	49



## ABSTRACT

The exposure of metals to corrosive fluids have resulted in their deterioration and total collapse, hence, the use of inhibitors to prevent and control corrosion. Inhibitors with weak adsorptive properties and high toxicity are less effective in inhibiting corrosion. This has influenced the use of green organic chemicals from plants as suitable inhibitors for corrosion in metals because they are eco-friendly and possess strong adsorptive properties. Rosemary oil, an extract from rosemary plant is known for its strong adsorption properties on metallic surfaces. Previous studies have reported the inhibition effect of rosemary oil on metals in different corrosive environments. This research aimed to minimise the corrosion in carbon steel using rosemary oil in solutions of citric acid, sulphuric acid and sodium chloride at ambient temperature using weight loss and potentiodynamic polarization techniques. Weight loss technique was carried out for a period of 21 days. The steel samples were immersed in citric acid, sulphuric acid and sodium chloride solutions. After 24 hours, the samples were taken out of the solutions, washed in acetone, rinsed in distilled water and air-dried for about an hour. The samples were re-weighed and re-immersed into the solutions. Potentiodynamic polarisation was carried out through the aid of the potentiostat with potential scans of -1.5 V to +1.75 V at a scan rate of 0.0015 V/s for a duration of 30 minutes. After each scan, the electrodes were polished with silicon carbide paper for easy flow of current. Adsorption of rosemary oil onto the steel surface fitted into the Langmuir model. Inhibition efficiencies of 98 %, 88 % and 78 % were obtained in sodium chloride, citric acid and sulphuric acid solutions which showed that rosemary oil is highly effective. Rosemary oil produced the highest inhibition efficiency in sodium chloride because of its low corrosive nature. Potentiodynamic plots reveal a cathodic-type inhibitor in sulphuric acid because the corrosion potential shifted more towards the negative potential. A mixed- type inhibitor in citric acid and sodium chloride solutions was observed because the corrosion potential shifted towards the positive and negative potentials. The Gibbs energy obtained in citric acid solution, sulphuric acid and sodium chloride solutions were less than -40 KJmol<sup>-1</sup>. This indicates that the inhibition mechanism of rosemary oil were physically adsorbed on carbon steel surface in the three solutions.

**Keywords;** Rosemary oil, Carbon Steel, Corrosion, Adsorption, Inhibition