

**MECHANICAL AND CORROSION BEHAVIOUR OF LOW CARBON STEEL IN
CRUDE OIL INHIBITED BY SOME EXTRACTS OF *Acacia Nilotica* (GUM ARABIC
TREE) PLANT.**

BY

NUNAYA DAVID FACI

**DEPARTMENT OF MECHANICAL ENGINEERING,
FACULTY OF ENGINEERING,
AHMADU BELLO UNIVERSITY, ZARIA.
NIGERIA**

SEPTEMBER, 2015

**MECHANICAL AND CORROSION BEHAVIOUR OF LOW CARBON STEEL IN
CRUDE OIL INHIBITED BY SOME EXTRACTS OF *Acacia Nilotica*(GUM ARABIC
TREE) PLANT.**

BY

NUNAYA DAVIDFACI(B.Eng, A.B.U)

MSc/ENG/866/2011-2012

**A DISSERTATION SUBMITTED TO THE SCHOOL OF POSGRADUATE
STUDIES,**

AHMADU BELLO UNIVERSITY, ZARIA

**IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF
MASTER OF SCIENCE DEGREE MECHANICAL IN ENGINEERING**

DEPARTMENT OF MECHANICAL ENGINEERING,

FACULTY OF ENGINEERING,

AHMADU BELLO UNIVERSITY, ZARIA.

NIGERIA

SEPTEMBER, 2015

DECLARATION

I declare that the work in this Dissertation entitled “Mechanical and Corrossion Behaviour of low carbon steel in crude oil inhibited by some extracts of *acacia nilotica* plant” has been carried out by me in the Department of Mechanical Engineering. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other Institution

FACI, Nunaya David

Signature

Date

CERTIFICATION

This dissertation entitled MECHANICAL AND CORROSION BEHAVIOUR OF LOW CARBON STEEL IN CRUDE OIL INHIBITED BY SOME EXTRACTS OF ACACIA NILOTICA PLANT by NUNAYA FACI meets the regulations governing the award of the of master of sciencedegree in Mechanical engineering of the Ahmadu Bello University and is approved for its contribution to knowledge and literary presentation.

Dr D.S Yawas

Chairman, supervisory committee

(Signature)

Date

Prof.A.I Obi

Member, supervisory committee

(signature)

Date

Dr .M. Dauda

Head of Department

(Signature)

Date

Prof Kabir Bala

Dean, School of Postgraduate Studies

(Signature)

Date

DEDICATION

This research work is dedicated to God Almighty the Alpha and Omega.

ACKNOWLEDGMENTS

I am sincerely grateful to God Almighty who had made all things possible. I will like to appreciate my major supervisor Dr D. S. Yawas for his guidance, words of advice and encouragement through out this work, I am grateful sir. I am also grateful to my minor supervisor Prof A .I. Obi for his support.

My profound gratitude goes to my able and respected parents Mr and Mrs David Faci for their moral, spiritual and financial support giving to me through out my academic career. Thank you, you are parents indeed. I sincerely appreciate my siblings Nachana'a, Adana'a and Ataitiya for being there for me.

I remain indebted to my father in the Lord Mr Irimiya Akawu and his family for providing a home for me away from home I am very grateful, may the love of God that brought us together abound in us forever. To my family of faith Chapel of Peace, I say you are the best, may the Lord keep you strong to the glory of his name.

Without reservations I appreciate the assistance I received from the staff members of mechanical engineering, Engr Kuburi Laminu, Mr. Sumaila, Mr. Muazu to mention but a few, members of staff of chemistry department NILEST, Mr Akawu, Mr Cletus, Mr Collins, Mr Pascal and Mr Abraham, I am most grateful to you all.

My deep gratitude also extends to my friends Adegoke, Julius, Iorpenda, Dajok, Omale, Sanda Abdulfatai, Aderemi and to all my colleagues for their support, criticism and encouragement. May God guide us in all our endeavours.

ABSTRACT

Five different parts of *Acacia nilotica* plant (leaves, pods, seed, bark and root) were subjected to the following analyses; extraction, phytochemical screening, corrosion inhibition test of low carbon steel in crude oil using gravimetric analyses, mechanical properties and surface morphology evaluation of the samples. The corrosion rate of low carbon steel specimen in the plant extract was found to decrease with immersion time (120hrs-792hrs) and with increase in concentration of the inhibitor (400ppm-1000ppm). The results further showed a decrease in inhibition efficiency (IE) of the inhibitor at elevated temperatures (40°C, 50°C, 60°C) indicating a physisorption of extracts on the carbon steel surface. The result from the mechanical properties (tensile, hardness and impact) evaluation showed higher values (741MN/m², 98.2HRB and 11.52J) for the inhibited samples than the uninhibited (692MN/m², 92.6HRB, 11.11J). The values of activation energy, free energy of adsorption and heat of adsorption of all the inhibitors were calculated in order to investigate the mechanism of corrosion inhibition. Adsorption on low carbon steel was found to obey the Langmuir adsorption isotherm. All the parts of the plant showed good inhibition efficiency in the medium ranging from 56.64% to 98.78% but the pod was the best with inhibitor efficiency of 98.78%.

TABLE OF CONTENTS

Cover page.....	i
Title page	ii
Declaration	iii
Certification	iv
Dedication.....	v
Acknowledgments	vi
ABSTRACT	vii
TABLE OF CONTENTS.....	viii
LIST OF TABLE	xi
LIST OF FIGURES	..xiii
LIST OF PLATES	.xvi
CHAPTER ONE.....	1
1.0 INTRODUCTION	.1
1.1 Background of study	.1
1.2 Statement of problem	.1
1.3 Present Resarch	.2
1.4 Aim and objectives	.3
1.5 Significance of the Study	3
1.6 Justification of Research	4
1.7 Scope of the study.....	5
CHAPTER TWO	6
2.0 LITERATURE REVIEW	6
2.1 Corrosion	6
2.2 Classification of Corrosion	8
2.2.1 Dry Corrosion	8
2.2.2 Wet Corrosion	8
2.3 Forms of Corrosion	8
2.3.1 Uniform Corrosion	9
2.3.2 Galvanic or Two Metal Corrosion.....	9
2.3.3 CO ₂ Corrosion	10
2.3.4 Crevice Corrosion	11
2.3.5 Intergranular Corrosion	12

2.3.6 Selective Leaching	12
2.3.7 Erosion Corrosion	12
2.3.8 Stress Corrosion	13
2.4 The Problem of Corrosion	14
2.5 Corrosion Inhibitors	15
2.5.1 Types of Corrosion Inhibitors	16
2.5.2 Organic Inhibitors	16
2.5.3 Green Corrosion Inhibitor	17
2.6 Acacia nilotica	18
2.6.1. Plant description	18
2.7 Review of Past Works	20
CHAPTER THREE	22
3.0 EQUIPMENT, MATERIALS AND EXPERIMENTAL PROCEDURE	22
3.1 Equipment	22
3.2 Materials	22
3.3 Experimental Procedure	23
3.3.1 Preparation of Specimen	23
3.3.2 Area and density of specimen.....	23
3.3.3 Preparation of Acacia plant extracts	24
3.3.4 Phyto-Chemical Analysis	26
3.3.5 Weight Loss Measurements	29
3.3.6 Effect of Temperature	30
3.4 Microstructure Examination	34
3.5 Mechanical Properties	35
3.5.1 Tensile Strength	35
3.5.2 Impact	35
3.5.3 Hardness	36
CHAPTER FOUR	37
4.0 RESULTS AND DISCUSSION.....	37
4.1 Results	37
4.1.1 Results obtained from corrosion test	39
4.2 Discussions.....	60

4.2.1 Phytochemical Analysis of the extracts	60
4.2.2 Corrosion Rate	60
4.2.3 Inhibition Efficiency	61
4.2.4 Effect of Temperature	61
4.2.5 Activation energy	61
4.2.6 Enthalpy and entropy of adsorption.....	62
4.2.7 Adsorption Isotherm.....	62
4.2.8 Free energy of adsorption.....	
634.2.9 Impact Strength, Tensile Strength and Hardness of the Specimens.....	
63	
4.3 Surface Studies by Scanning Electron Microscopy	64
CHAPTER FIVE 64	
5.0 CONCLUSION AND RECOMMENDATIONS 64	
5.1 Conclusions 64	
5.2 Recommendations 65	
REFERENCES 66	
APPENDICES.....	72

LIST OF TABLES

Table 1 Elemental composition of low carbon steel	72
Table.2 Phytochemical Tests	73
Table 3: Corrosion rate of low carbon steel in crude oil in the absence of inhibitor	74
Table 4: Corrosion rate of low carbon steel + crude oil + 1000ppm root extract.	74
Table 5: Corrosion rate of low carbon steel + crude oil + 800ppm root extract.	75
Table 6: Corrosion rate of low carbon steel+ crude oil + 600ppm root extract	75
Table 7: Corrosion rate of low carbon steel + crude oil + 400ppm root extract	76
Table 8: Corrosion rate of low carbon steel + crude oil + 1000ppm leaves extract	76
Table9 : Corrosion rate of low carbon steel + crude oil + 800ppm leaves extract	77
Table 10: Corrosion rate of low carbon steel + crude oil + of 600ppm leaves extract	77
Table 11: Corrosion rate of low carbon steel in crude oil + 400ppm leaves extract	78
Table 12: Corrosion rate of low carbon steel + crude oil + 1000ppm pods extract	78
Table 13: Corrosion rate of low carbon steel+ crude oil + 800ppm pods extract	79
Table 14: Corrosion rate of low carbon steel + crude oil + 600ppm pods extract	79
Table 15: Corrosion rate of low carbon steel + crude oil + 400ppm pods extract	80
Table 16: Corrosion rate of low carbon steel+ crude oil + 1000ppm bark extract	80
Table 17: Corrosion rate of low carbon steel + crude oil + 800ppm bark extract	81
Table 18: Corrosion rate of low carbon steel + crude oil + 600ppm bark extract	81
Table 19: Corrosion rate of low carbon steel + crude oil + 400ppm bark extract	82
Table 20: Corrosion rate of low carbon steel + crude oil + 1000ppm seed extract	82
Table 21: Corrosion rate of low carbon steel + crude oil + 800ppm seed extract	83
Table 22: Corrosion rate of low carbon steel + crude oil + 600ppm seed extract	83
Table 23: Corrosion rate of low carbon steel+ crude oil + 400ppm seed extract	84
Table 24: Degree of surface coverage (θ) and percentage inhibition efficiency (% IE) of Root in crude oil at 303-313 K	85
Table 25: Degree of surface coverage (θ) and percentage inhibition efficiency (% IE)	

of Pods in Crude oil at 303-313 K	86
Table 26: Degree of surface coverage (θ) and percentage inhibition efficiency (% IE) of Leaves in Crude oil at 303-313 K	87
Table 27: Degree of surface coverage (θ) and percentage inhibition efficiency (% IE) of Bark in Crude oil at 303-313 K	88
Table 28: Degree of surface coverage (θ) and percentage inhibition efficiency (% IE) of Seed in Crude oil at 303-313 K	89
Table 29: Values of activation parameters of Root on the surface of steel in Crude oil	90
Table 30 Values of activation parameters of Pods on the surface of steel in Crude oil	90
Table 31 Values of activation parameters of Leaves on the surface of steel in Crude oil	91
Table 32 Values of activation parameters of Seed on the surface of steel in Crude	91
Table 33 Values of activation parameters of Bark on the surface of steel in Crude oil	92
Table 34: Values of thermodynamic parameters (Langmuir adsorption isotherm) for adsorption of Root in Crude oil	92
Table 35: Values of thermodynamic parameters (Langmuir adsorption isotherm) for adsorption of Bark in Crude oil	93
Table 36: Values of thermodynamic parameters (Langmuir adsorption isotherm) for adsorption of Pods in Crude oil	93
Table 37: Values of thermodynamic parameters (Langmuir adsorption isotherm) for adsorption of Leaves in Crude oil	94
Table 38: Values of thermodynamic parameters (Langmuir adsorption isotherm) for adsorption of Seed in Crude oil	94
Table 39 Impact test result of Samples from the 1000ppm concentration after 33days	95
Table 40 Tensile test result of Samples from the 1000ppm concentration after 33days	95
Table 41: Rockwell Hardness Number ForThe Samples of 1000ppm after 33days	96

LIST OF FIGURES

Fig. 4.1: Variation of Corrosion rate with exposure time of low carbon steel in crude oil in blank and presence of 1000ppm concentration of plant extracts.	41
Fig. 4.2: Variation of Corrosion rate with exposure time of low carbon steel in crude oil in blank and presence of 800ppm concentration of plants extracts	41
Fig. 4.3: Variation of Corrosion rate with exposure time of low carbon steel in crude oil in blank and presence 600ppm concentration of extracts.	42
Fig. 4.4: Variation of Corrosion rate with exposure time of low carbon steel in crude oil in blank and presence of 400ppm concentration of extracts.	42
Fig.4.5: Variation of %IE with inhibitor concentration in crude oil at 30°C after 5days	43
Fig.4.6: Variation of %IE with inhibitor concentration in crude oil at 30°C after 12days	43
Fig.4.7: Variation of %IE with inhibitor concentration in crude oil at 30°C after 19days	44
Fig.4.8: Variation of %IE with inhibitor concentration in crude oil at 30°C after 26days	44
Fig.4.9: Variation of %IE with inhibitor concentration in crude oil at (30°) after 33days.	45
Fig.4.10: Variation of %IE with temperature for low carbon steel in crude oil in the presence of various concentration of root extract.	45
Fig.4.11: Variation of %IE with temperature for low carbon steel in crude oil in the presence of various concentration of pods extract	46
Fig.4.12: Variation of %IE with temperature for low carbon steel in crude oil in the presence of various concentration of leaves extract.	46
Fig.4.13: Variation of %IE with temperature for low carbon steel in crude oil in the presence of various concentration of bark extract	47
Fig.4.14: Variation of %IE with temperature for low carbon steel in crude oil in the presence of various concentration of seed extract .	47
Fig. 4.15: Arrhenius plot for low carbon steel in crude oil in the blank and presence of various concentration of root extract.	48

Fig. 4.16: Arrhenius plot for low carbon steel in crude oil in the blank and presence of various concentration of pods extract.	48
Fig. 4.17: Arrhenius plot for low carbon steel in crude oil in the blank and presence of various concentration of leaves extract.	49
Fig. 4.18: Arrhenius plot for low carbon steel in crude oil in the blank and presence of various concentration of bark extract.	49
Fig. 4.19: Arrhenius plot for low carbon steel in crude oil in the blank and presence of various concentration of seed extract.	50
Fig. 4.20: Plot of $\log (CR/T)$ against $1/T$ for the corrosion of low carbon steel in crude oil in the blank and presence of different concentrations of root extract.	50
Fig. 4.21: Plot of $\log (CR/T)$ against $1/T$ for the corrosion of low carbon steel in crude oil in the blank and presence of different concentrations of pod extract.	51
Fig. 4.22: Plot of $\log (CR/T)$ against $1/T$ for the corrosion of low carbon steel in crude oil in the blank and presence of different concentrations of leaves extract.	51
Fig. 4.23: Plot of $\log (CR/T)$ against $1/T$ for the corrosion of low carbon steel in crude oil in the blank and presence of different concentrations of bark extract.	52
Fig. 4.24: Plot of $\log (CR/T)$ against $1/T$ for the corrosion of low carbon steel in crude oil in the blank and presence of different concentrations of seed extract.	52
Fig. 4.25: Plot of C/θ against C for corrosion of low carbon steel in crude oil at different concentration of root extract.	53
Fig. 4.26: Plot of C/θ against C for corrosion of low carbon steel in crude oil at different concentration of leaves extract.	53
Fig. 4.27: Plot of C/θ against C for corrosion of low carbon steel in crude oil at different concentration of pod extract.	54
Fig. 4.28: Plot of C/θ against C for corrosion of low carbon steel in crude oil at different concentration of bark extract.	54
Fig. 4.29: Plot of C/θ against C for corrosion of low carbon steel in crude oil at different concentration of seed extract.	55
Fig. 4.30: Impact energy for samples from 1000ppm of all the extract after 33days	55

Fig. 4.31: Tensile strength for samples from 1000ppm of all the extract after 33days 56

Fig. 4.32: Hardness value for samples from 1000ppm of all the extract after 33days 56

LIST OF PLATES

Plate; I: Acacia Pods and Seeds	12
Plate; II: Acacia Flowers and leaves	12
Plate; III: Acacia Stem and Bark	13
Plate;IV: soxhlet extractor	17
Plate V: Experimental setup.	20
Plate VI: SEM micrograph of low carbon steel in crude oil	57
PlateV II. SEM micrograph of low carbon steel in crude oil + 1000ppm of root extract	57
PlateV III: SEM micrograph of low carbon steel in crude oil + 1000ppm of pod extract	58
Plate IX: SEM micrograph of low carbon steel in crude oil + 1000ppm of leave extract	58
PlateX. SEM micrograph of low carbon steel in crude oil + 1000ppm of bark extract	59
Plate XI: SEM micrograph of low carbon steel in crude oil + 1000ppm of seed extract	59

LIST OF APPENDICES

Appendix I:Results of Weight loss Analysis at Elevated Temperature.....	72
Appendix II :Results of Weight loss Analysis at Elevated Temperature.....	83
Appendix III :Results of Adsorption and thermodynamic analysis.....	88
Appendix IV:Results of Mechanical Properties.....	93

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of study

Pipelines play an extremely important role all over the world as a means of transporting gases and liquid over long distances from their sources to ultimate consumers. So corrosion problem exist in the oil industry at every stage of production from initial extraction to refining and storage prior to use requiring the application of corrosion inhibitors (Migahed, 2005).

One of the serious problems of oil extracting industry is the corrosion process. The successful application of carbon steels in oil and gas pipelines depends mainly on either the formation of protective corrosion product film or the use of corrosion inhibitors (Hany et al., 2012)

Corrosion prevention is an important aspect of oil and gas production. The pipelines are protected from internal corrosion by the application of corrosion inhibitors. In recent years the application of 'green chemistry' principles to the area of corrosion inhibitors has attracted lot of attention which has resulted in the reduction/elimination of toxic inhibitors and the production of 'green' or low toxic environmentally friendly formulations. A number of corrosion inhibitors have been developed with low environmental impact while preserving the inhibitor efficiency (Shaheen et al., 2006)

1.2 Statement of problem

Corrosion is an increasingly serious and costly problem that can lead to plant and equipment failures, leakages in oil and gas pipelines as well as steel bridges, ship, and buildings. These failures range from being an annoyance to being catastrophic. Failures caused by corrosion could and do lead to a direct failure of a component which could affect the entire system and

can not only be very expensive in terms of down time to repair or replace plant and equipment, but can also prove to be very costly in loss of productivity both to human life and health as well as to the environment (www.corr-ex.com/library_corrosion_control, 2013). Organic compounds containing nitrogen, sulfur and oxygen have long been used as potential corrosion inhibitors (Mobin et al., 2011). These compounds get adsorbed, form a protective layer or insoluble complex on the metal surface and block the active corrosion sites. However, most of these compounds are synthetic chemicals, expensive and very hazardous to both human beings and the environments and needs to be replaced with nontoxic and eco-friendly compounds. Over the years, numerous classes of organic compounds have been investigated as corrosion inhibitors. However the trend in green chemistry is concentrated towards the replacement of most of these inhibitors with nontoxic, cheap and eco-friendly compounds. In recent years, a number of eco-friendly corrosion inhibitors have been exploited as green alternative to toxic and hazardous compounds (Mobin et al., 2011). *Acacia nilotica* has been established as a very important plant since early times as source of tannin (Gupta, 1970) but has not been maximally utilized.

1.3 Present Research

In this research, extracts from *acacia nilotica* pod, leaves, bark, seed and, were used as corrosion inhibitor for low carbon steel in crude oil. The test specimen were brought out of the test media at various intervals and corrosion rate (C.R) was determine through weight loss analysis, the inhibitor efficiency, film attractive power, activation energy and enthalpy of adsorption of the inhibitors were calculated using the require expression and relationship. The surface condition of the samples were examined using scanning electron microscope, the mechanical properties were also evaluated.

1.4 Aim and Objectives

The aim of this research is to carry out a performance evaluation on the extracts of *Acacia nilotica* plant (pods, bark, roots, leaves and seed) as a corrosion inhibitor for low carbon steel in crude oil. The specific objectives are to:

I Carry out Phyto-chemical (tannins, alkaloids and flavours) analyses of the plant extracts.

II Carry out corrosion test using weight loss technique by varying concentration of inhibitors and temperature.

III Analyze the kinetic and thermodynamic parameters of the inhibitor in the aggressive medium

IV Evaluate the mechanical properties (tensile, hardness and impact) of the sample.

V Examination of the metal surface in contact with crude oil with and without the inhibitors using SEM

1.5 Significance of the Study

1. Development of effective and environmentally acceptable corrosion inhibitors as alternatives to toxic and carcinogenic ones are being researched into for present research interest (Loto, 2012).

2. Most of the corrosion inhibitors are synthetic chemicals, expensive and very hazardous to environment. Therefore, it is desirable to source for environmentally friendly inhibitors (Paul, 2012).

3. Owing to the increasing ecological awareness as well as the strict environmental regulations, and consequently the need to develop environmentally friendly processes,

attention is currently focused on the development of “green” alternatives to mitigating corrosion. (Special Issue on Green approaches to corrosion mitigation, 2011).

4. Carbon steel is widely used as the constructional material in most of the major industries particularly in petroleum, power production, chemical and electrochemical industries, especially due to its excellent mechanical properties and low cost. Corrosion of carbon steel is a significant problem in the oil& gas production and transportation systems, which causes significant economic loss (Song et al., 2004). As a result of corrosion rupture of the pipe wall frequently causes failure of petroleum and gas pipelines. The breakdowns are followed by large losses of the products, environmental pollution and ecological disasters (Mikhailovskii et al., 1997). The majority of oil and gas pipelines failures result from carbon dioxide corrosion of carbon and low alloy steels (Lopez et al., 2003). It occurs at all stages of production from down hole to surface equipment and processing facilities.

1.6 Justification of Research

This work is no doubt justifiable owing to the increasing ecological awareness as well as the strict environmental regulations, and consequently the need to develop environmentally friendly processes, attention is currently focused on the development of “green” alternatives to mitigating corrosion in which the leaves,pods,roots, bark and seed of acacia nilotica happen to fall into this category. The leaves, pods, roots,bark and seed of this plant are not edible. Hence, it is most appropriate to utilize this plant in the production of corrosion inhibitors which will compete or totally replaced some organic and inorganic chemical corrosion inhibitors which are hazardous and toxic to human and the environment (Special bulletin on Green approaches to corrosion mitigation, 2011).

1.7 Scope of the Study

This Study was limited to investigation of inhibitory effectiveness of *Acacia nilotica* plant extracts (pods, seed, leaves, bark and roots) on low carbon steel in crude oil using weight loss method in the presence of each inhibitor at various temperatures. The mechanical properties were evaluated and the surface morphology of the sample was examined using scanning electron microscope (SEM).

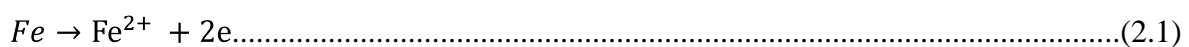
CHAPTER TWO

2.0 LITERATURE REVIEW

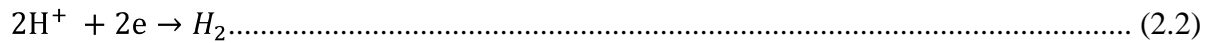
2.1 Corrosion

Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals. Virtually all corrosion reactions are electrochemical in nature, at anodic sites on the surface the iron goes into solution as ferrous ions, this constituting the anodic reaction. As iron atoms undergo oxidation to ions they release electrons whose negative charge would quickly build up in the metal and prevent further anodic reaction, or corrosion. Thus this dissolution will only continue if the electrons released can pass to a site on the metal surface where a cathodic reaction is possible. At a cathodic site the electrons react with some reducible component of the electrolyte and are themselves removed from the metal. The rates of the anodic and cathodic reactions must be equivalent according to Faraday's Laws, being determined by the total flow of electrons from anodes to cathodes which is called the "corrosion current", I_{cor} . Since the corrosion current must also flow through the electrolyte by ionic conduction the conductivity of the electrolyte will influence the way in which corrosion cells operate. The corroding piece of metal is described as a "mixed electrode" since simultaneous anodic and cathodic reactions are proceeding on its surface. The mixed electrode is a complete electrochemical cell on one metal surface.

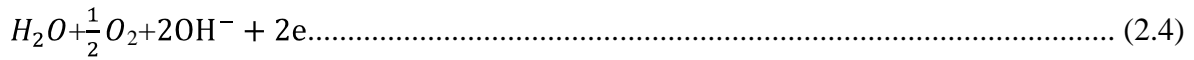
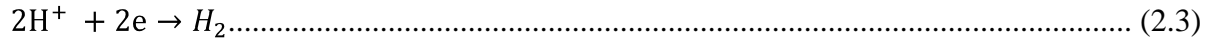
The most common and important electrochemical reactions in the corrosion of iron are the Anodic Reaction (Bill and Gareth,2003)



Cathodic reaction

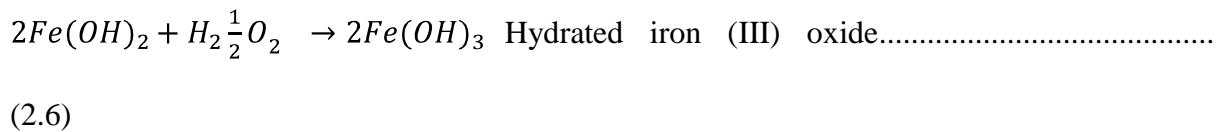


Cathodic reaction(simplified)

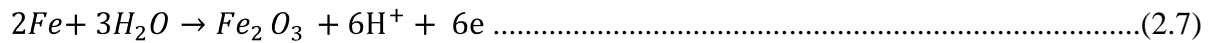


Reaction in equation 2.3 is mostcommon in acids and in the pH range 6.5 – 8.5 the most important reaction is oxygen reduction in equation 2.4 in this latter case corrosion is usually accompanied by the formation of solid corrosion debris from the reaction between the anodic and cathodic products.(Bill and Gareth, 2003):

Pure iron (II) hydroxide is white but the material initially produced by corrosion is normally a greenish colour due to partial oxidation in air.



Further hydration and oxidation reactions can occur and the reddish rust that eventually forms is a complex mixture whose exact constitution will depend on other trace elements which are present. Because the rust is precipitated as a result of secondary reactions it is porous and absorbent and tends to act as a sort of harmful poultice which encourages further corrosion. For other metals or different environments different types of anodic and cathodic reactions may occur. If solid corrosion products are produced directly on the surface as the first result of anodic oxidation these may provide a highly protective surface film which retards further corrosion, the surface is then said to be “passive”. An example of such a process would be the production of an oxide film on iron in water, a reaction which is encouraged by oxidizing conditions or elevated temperatures (Bill and Gareth, 2003).



2.2 Classification of Corrosion

Corrosion is classified into many different ways. The preferred classification of corrosion is given below (Fontana, 1987):

2.2.1 Dry Corrosion

This type of corrosion takes place in the absence of a liquid phase or above the dew point of the environment. Vapours and gases are usually the corrodents. Dry corrosion is often associated with high temperature; a good example is the attack on steel by furnace.

2.2.2 Wet Corrosion

Wet corrosion takes place when a liquid is present. It usually involves an aqueous solution or electrolyte. This is the most common type of corrosion. A good example is corrosion of turbine blade by water.

2.3 Forms of Corrosion

It is convenient to classify corrosion by the forms in which it manifests itself, the basis for this classification being the appearance of the corroded metal. Each form can be identified by mere visual observation. In most cases the naked eye is sufficient, but sometimes magnification is helpful or required. (Callister, 2003).

Some of the eight forms of corrosion are unique, but all of them are more or less interrelated. The eight forms are: (1) Uniform, or general attack, (2)Galvanic, or two-metal corrosion, (3) crevice corrosion, (4) Carbon dioxide corrosion (5) Intergranular corrosion (6) Selective leaching or parting, (7) Erosion corrosion, and (8)Stress corrosion. This listing is arbitrary

but covers practically all corrosion failures and problems. The forms are not listed in any particular order of importance.

Below, the eight forms of corrosion are discussed in terms of their characteristics, mechanisms, and preventive measures.

2.3.1 Uniform Corrosion

Uniform corrosion as the name suggests, occurs over the majority of the surface of a metal at a steady and often predictable rate. Its predictability facilitates easy control, the most basic method being to make the material thick enough to function for the lifetime of the component. (Bill and Gareth, 2003)

Uniform corrosion can be slowed or stopped by using five basic facts;

(1) Slow down or stop the movement of electrons
(a) Protective coating
(b) Reduce the conductivity of the solution in contact with the metal, an extreme case being to keep it dry. Wash away conductive pollutants regularly.
(c) Cathodic protection

(2) Slow down or stop oxygen from reaching the surface.

(3) Prevent the metal from giving up electrons by using a more corrosion resistant metal higher in the electrochemical series. Use a sacrificial coating which gives up its electrons more easily than the metal being protected. Apply cathodic protection. Use inhibitors.

(4) Select a metal that forms an oxide that is protective and stops the reaction.

(5) Control and consideration of environmental and thermal factors is also essential.

2.3.2 Galvanic or Two Metal Corrosion

This can occur when two different metals are placed in contact with each other and is caused by the greater willingness of one of the metal to give up electrons than the other (Bill and Gareth, 2003). A potential difference usually exists between two dissimilar metals when they are immersed in a corrosive or conductive solution. (Fontana., 1987).

A number of procedures or practices can be used for combating or minimizing galvanic corrosion. Sometimes one is sufficient, but a combination of one or more may be required.

These practices are as follows:

- (i) Select combination of metals as close together as possible in the galvanic series.
- (ii) Avoid the unfavorable area effect of a small anode and large cathode.
- (iii) Insulate dissimilar metals wherever practicable.
- (iv) Apply coatings with caution.
- (v) Use inhibitors
- (vi) Avoid threaded joints for materials far apart in the series (Fontana, 1987).

2.3.3 Carbon dioxide Corrosion

Carbon dioxide corrosion or sweet corrosion is the corrosion of carbon and low alloy steel by carbonic acid and its derivatives. Carbonic acid is formed by gaseous carbon dioxide first dissolving into water, and then reacting to it. There are three main types of carbon dioxide induced corrosion in pipelines: (Hany et al., 2012)

Pitting Corrosion: Pitting corrosion, also simply known as pitting, is an extremely localized form of corrosion that occurs when a corrosive medium attacks a metal at specific points causing small holes or pits to form. This usually happens when a protective coating or oxide film is perforated, due to mechanical damage or chemical degradation. Pitting can be one of the most dangerous forms of corrosion because it is difficult to anticipate and prevent,

relatively difficult to detect, occurs very rapidly, and penetrates a metal without causing it to lose a significant amount of weight (Benjamin *et al.*,2006).

Pitting Corrosion can be prevented or reduced by:

- I. Proper selection of materials.
- II. The use of inhibitors.
- III. Application of protective coating and cathodic protection.

Mesa-Type Attack: Mesa attack is a type of localized corrosion and happens in low to medium conditions where the protective ion carbonate film forms but it is unable to bear the operating flow regime.

Flow-Induced Localized Corrosion: This kind of corrosion happens in areas of transient and turbulent flow and it is when the protective barrier covering the pipe wall is stripped away, leaving a small exposed area for where all corrosion activities take place

2.3.4 Crevice Corrosion

If two areas of a component in close proximity differ in the amount of reactive constituent available the reaction in one of the areas is speeded up. An example of this is crevice corrosion which occurs when oxygen cannot penetrate a crevice and a differential aeration cell is set up, Corrosion occurs rapidly in the area with less oxygen (Bill and Gareth, 2003).

Some methods and procedures for combating or minimizing crevice corrosion are as follows:

- (i) Use welded butt joints instead of riveted or bolted joints in new equipment.
- (ii) Avoiding sharp corners and designing out stagnant areas
- (iii) Close crevices in existing lap joints by continuous welding or soldering
- (iv) Inspect equipment and remove deposits frequently.

- (v) Remove solids in suspension early in the process or plant flow sheet, if possible.
- (vi) Remove wet packing materials during long shutdowns.
- (vii) Use “solid” nonabsorbent gaskets, wherever possible.
- (viii) Selection of resistant materials like titanium-0.15 percent palladium (Ti-0.15Pd)

2.3.5 Intergranular Corrosion

Intergranular corrosion is the preferential attack of the grain boundaries of the crystals that form the metal. It is caused by the physical and chemical differences between the centres and edges of the grain (Bill and Gareth, 2003).

Intergranular corrosion can be avoided by type:

(1) Selection of stabilized grades alloyed with titanium (for example type 321) or niobium (for example type 347).

(2) Control of heat treatments and processing to avoid susceptible temperature range.

2.3.6 Selective Leaching

This type of corrosion occurs when one component or phase in a solid alloy is more susceptible to attack than another and corrodes preferentially leaving a porous material that crumbles (Bill and Gareth, 2003). Corrosion by selective leaching is best avoided by selection of a resistant material but other means can be effective such as:

- (i) Coating the material
- (ii) Reducing the aggressiveness of the environment
- (iii) Use of cathodic protection

2.3.7 Erosion Corrosion

Erosion corrosion is the acceleration or increase in rate of deterioration or attack on a metal because of relative movement between a corrosion fluid and the metal surface. The protective layers and corrosion products of the metal are continually removed exposing fresh metal to corrosion (Fontana, 1987).

Prevention or minimization of this type of corrosion can be achieved by:

- (i) Materials with better resistance to erosion corrosion like 2.25Cr-1Mo steel and austenitics.
- (ii) Reducing the flow rate and turbulence
- (iii) Employ proper design features for the anticipated forms of corrosion.
- (iv) Alteration of the environment
- (v) Coating
- (vi) Cathodic protection
- (vii) Use of replaceable or robust linings in susceptible areas.

2.3.8 Stress Corrosion

Stress corrosion cracking (SCC) refers to cracking caused by the simultaneous presence of tensile stress and a specific corrosive medium which eventually leads to the catastrophic failure of the component.(Fontana, 1987).

Stress-corrosion cracking may be reduced or prevented by application of one or more of the following methods (Fontana, 1987):

- (i) Lowering the stress below the threshold value
- (ii) Design to minimize thermal and residual stresses.
- (iii) Eliminating the critical environment specie
- (iv) Developing compressive stresses in the surface the material.

- (v) Selection of a suitable material not susceptible to the environment.
- (vi) Applying cathodic protection.
- (vii) Adding inhibitors to the system if feasible.
- (viii) Coatings are sometimes used.

2.4 The Problem of Corrosion

Corrosion is one of the serious problems of oil industry. The successful application of carbon steels in oil and gas pipelines and production tubular in Carbon Dioxide (CO₂) containing environments depends mainly on either the formation of protective corrosion product film or the use of corrosion inhibitors(Hany et al.,2012) The destructive tendency of corrosion is not only limited to the oil and gas industries, but industries such as: Construction industries, automobile industries, water treatment plant, Chemical plant, machinery, reaction etc. Apart from the heavy economic losses incurred as a result of corrosion, some harmful or disastrous effects of corrosion are as follows:

1. Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown,when the metal is lost in localized zones so as to give a crack like structure, very considerable weakening may result from quite a small amount of metal loss.
2. Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges, cars, aircraft).
3. Reduced value of goods due to deterioration.
4. Contamination of fluids in vessels and pipes.

5. Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings. For example corrosive sea water may enter the boilers of a power station if the condenser tubes perforate.

6. Loss of technically important surface properties of a metallic component. These could include frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.

7. Mechanical damage to valves, pumps, etc., or blockage of pipes by solid corrosion products.

2.5 Corrosion Inhibitors

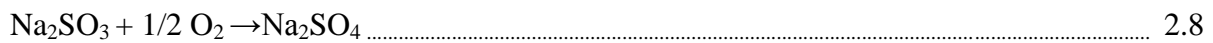
An inhibitor is a substance that, when added in small concentrations, decreases the effective corrosion rate. Inhibitors fall into four general categories based on mechanism and composition. These categories are 1) barrier layer formation, 2) neutralizing, 3) scavenging, and 4) other environmental modification. (Ernest, 2001)

Barrier Inhibitors:Barrier layer formation inhibitors form a layer on the corroding metal surface, modifying the surface to reduce the apparent corrosion rate. They represent the largest class of inhibitive substances. Adsorption-type inhibitors are the most common barrier layer inhibitors. In general, these organic compounds are adsorbed and form a stable bond with the metal surface. The apparent corrosion rate decreases as surface adsorption is completed (Ernest,2001)

Inhibitors Neutralizing: Neutralizing inhibitors reduce the hydrogen ion in the environment. Typical neutralizing inhibitors are amines, ammonia (NH₃), and morpholine. These inhibitors are particularly effective in boiler water treatment and weak acid solutions but have not been widely used on pipelines.

Scavenging Inhibitors: Scavenging inhibitors remove corrosive ions from solutions. Well-known scavenging inhibitors include hydrazine and sodium sulphite. These two inhibitors remove dissolved oxygen from treated boiler water. (Ernest, 2001)

Sodium sulphite reaction:



Hydrazine reaction:



2.5.1 Types of Corrosion Inhibitors

Several factors including cost and amount, easy availability and most important safety to environment and its species need to be considered when choosing an inhibitor.

Basically, they are two types of corrosion inhibitors; these are organic and inorganic corrosion inhibitors. But at the moment, an intensive research is being undertaken by researchers in the area of plants being used as a corrosion inhibitor due to its non-hazardous and non-toxic to human and the environment. Researchers are trying to classify corrosion inhibitor substances gotten from plant extracts (leaves, fruits, seed, bark) as green corrosion inhibitors. Under this heading, plants as a green corrosion inhibitor shall be briefly discussed.

2.5.1.1 Organic Inhibitors

Organic inhibitors generally have heteroatoms. O, N, and S are found to have high basicity and electron density and thus act as corrosion inhibitors. O, N, and S are the active centers for the process of adsorption on the metal surface. The inhibition efficiency should follow the sequence $\text{O} < \text{N} < \text{S} < \text{P}$. The use of organic compounds containing oxygen, sulphur, and especially nitrogen to reduce corrosion attack on steel has been studied in some detail. The

existing data show that most organic inhibitors adsorbed on the metal surface by displacing water molecules on the surface and forming a compact barrier. Availability of non-bonded (lone pair) and p-electrons in inhibitor molecules facilitate electron transfer from the inhibitor to the metal. A coordinate covalent bond involving transfer of electrons from inhibitor to the metal surface may be formed. The strength of the chemisorption bond depends upon the electron density on the donor atom of the functional group and also the Polaris ability of the group.(Fontana, 1987).

It is also known that most of the synthetic organic inhibitors have hazardous effect and there is the need to develop cheap, nontoxic and ecofriendly inhibitors, processes have now urged researchers to focus on the use of natural products (Rani and Basu, 2012).

2.5.1.3 Green Corrosion Inhibitor

Environmental concerns worldwide are increasing and are likely to influence the choice of corrosion inhibitors in the future. Some chemicals are excellent inhibitors, but are quite toxic and readily absorbed through the skin. The known hazardous effects of most synthetic organic inhibitors and restrictive environmental regulations have now made researchers to focus on developing cheap, non-toxic and environmental friendly natural products as corrosion inhibitors. Among the numerous organic compounds that have been tested and are applied industrially as corrosion inhibitors, those that are nontoxic are now far more strategic than in the recent past (Rani and Basu, 2012).

Green corrosion inhibitors (extract from plant) which happen to be a nontoxic organic compound, displaying substantially improved environmental properties will be the inhibitors most widely used in the future. These natural organic compounds are either synthesized or extracted from aromatic herbs, spices and medicinal plants. In the past two decades, the research in the field of “green” corrosion inhibitors has been addressed toward the goal of

using cheap, effective molecules at low or “zero” environmental impact. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost and are biodegradable in nature. The use of these natural products such as extracted compounds from leaves or seeds as corrosion inhibitors have been widely reported by several authors (Rani and Basu, 2012).

2.6. Acacia nilotica

Acacia nilotica is found in various parts of Nigeria spanning from the rainforest through the savannah up to the arid vegetation zones. It is seen to present itself as a highly economic plant, useful in the medical and agricultural fields. It has several engineering applications especially in corrosion inhibition. In this research, *Acacia* plant(i.e. Leaves, Seeds, Pods, Bark and Roots) will be investigated for its inhibition efficiency in crude oil.

2.6.1. Plant description

Acacia nilotica is a single stemmed plant, it grows to 15-18 m in height and 2-3 m in diameter. Pods and Seeds: Pods are 7-15 cm long, green and tomatoes (when immature) or greenish black (when mature), indehiscent, deeply constricted between the seed giving a necklace appearance. Seeds are 8-12 per pod, compressed, ovoid, dark brown shining with hard testa (Iman et al., 2007).



Plate; I: Acacia Pods and Seeds (Iman et al., 2007)

Leaves: The leaves are bipinnate, pinnate 3-10 pairs, 1.3- 3.8 cm long, leaflets 10-20 pairs, and 2-mm long (Beniwal et al., 1992).

Flowers: Flowers are globular heads, 1.2-1.5 cm in diameter of a bright golden yellow colour, develop either in axillary or whorly pattern on peduncles 2-3 cm long located at the end of branches (Bargal and Bargali, 2009).



Plate;II: Acacia Flowers and leaves (Bargal and Bargali, 2009)

Stem: Stems are usually dark to black colored, deep longitudinal fissured, grey-pinkish slash, exuding a reddish low quality gum (Brenan, 1983).

Bark: The bark a tinge of orange and/or green (young tree), but older trees have dark, rough bark and tend to lose their thorns (Khan et al., 2009).



Plate;III: Acacia Stem and Bark, (Khan et al., 2009)

Root: Root is generally of brown colour in older and whitish in younger regions.

2.7 Review of Past Works

Anafi and Obi (2004) investigated the corrosion inhibition of low carbon steel in simulated media by a Methanolic Extract of Bitter leaf. The solvent extract of bitter leaf was compared with sodium benzoate with low carbon steel immersed in sea water, 0.3 M H₂SO₄ and 0.3M HCl media at ambient temperature using weight loss method. They found out that the inhibition ability of bitter leaf against corrosion was best in sea water where it exhibited an inhibitive efficiency of 61.19%. Sodium benzoate however surpassed bitter leaf in its corrosion inhibition ability in all test media used in the investigation

Yawas (2005) made a suitability assessment of neem, mahogany, cashew, locust bean husk, and acacia nilotica pod extracts as corrosion inhibitors. Neem, sesame, mahogany, soyabean, cotton, and cracking groundnut seed oils were also analyzed. Inhibition efficiencies increased with increase in inhibitor concentrations and temperature but decreased in the case of cotton seed and sesame oil. It also showed the ability of the inhibitors to reduce stress corrosion of carbon steel in acidic media

Ita (2006) studied the inhibition of corrosion of low carbon steel in hydrochloric acid by isatin glycin (ING) and isatin (IN) at 30-60°C and concentrations of 0.0001 M to 0.0005 M via weight loss method. At the highest inhibitor concentration studied ING exhibited inhibition efficiency of 87% while IN exhibited 84% at 60°C. The difference in the inhibitory

properties of the inhibitors was explained in terms of the difference in their molecular structures and solubility rather than difference in molecular weights alone

Yoon-Seok and Srdjan(2010) determined the corrosive potential of Carbon dioxide transport pipeline in high $p\text{CO}_2$ -water environments.They evaluated the corrosive potential of carbon steel under high pressure CO_2 -water systems to simulate the condition of CO_2 transportation pipeline in the CO_2 capture and storage (CCS) applications.

Ndibe et al (2011) studied the corrosion inhibition of low carbon steel using acid extract of *Vernonia amygdalina* (VA) in HCl and HNO_3 using standard weight loss method. The studies were carried out at 30-60°C temperatures range in 0.1-0.5M concentrations of the acids using 0.01 – 0.03g/l concentrations of inhibitor. The results indicated that the rate of corrosion of the metal in the media increased with an increase in the concentration of the acid and decreased with an increase in the concentration of the inhibitor. VA is an adsorption inhibitor and its adsorption on the surface of low carbon steel is physically controlled, exothermic, spontaneous and sufficiently fits with langmuir adsorption isotherm.

Kuburi (2011) investigated the effect of flow velocity and exposure time on the corrosion rate of low carbon steel in crude oil. The study was performed using neem oil and locust bean husk extract as inhibitors. Results obtained showed a decrease in corrosion rate with time in uninhibited and inhibited systems but corrosion rate increases with increase in Reynolds number.

Hany et al(2012) reviewed corrosion protection of steel pipelines against Carbon dioxide CO_2 corrosion.They found that the successful application of carbon steels in oil and gas pipelines and production tubular in Carbon Dioxide (CO_2) containing environments depends inhibitors.

Ilyasu, (2012).Evaluated the susceptibility of austenitic stainless steel to stress corrosion cracking in some aggressive environment and found out that austentic stainless steel was resistance to general corrosion but susceptible to stress corrosion in NaCl environment and H₂SO₄with higher susceptibility in NaCl.

CHAPTER THREE

3.0 EQUIPMENT,MATERIALS AND EXPERIMENTAL PROCEDURE

3.1 Equipment

The equipment used for this research include the following

i Analytical mass balance:For weighing inhibitor plant powder and low carbon steel specimen

iiVenire Caliper: measuring dimension of coupons

iii Wire brush :For wire cleaning the specimens.

iv Beakers: Container for the experiment

V Soxhlet extractor :For extraction of plant

Vi Desiccator: Keep coupons in moisture free environment

Vii Scanning electron microscope: used for surface examination.

Viii Hounsfield tensometer (Tensile Testing Machine).

ix Hounsfield Impact Testing Machine.

x Indenter universal hardness testing machine

3.2 Materials

The materials used for this study included:

- i low carbon steel specimens(test coupons).
- ii Extracts from acacia leaves,pods,seeds, barks and roots.
- iii methanol
- iv Distilled water
- v Acetone
- vi Crude oil.

3.3 Experimental Procedure

3.3.1 Preparation of Specimen

The specimens were cut using a saw into the required dimension of 15x50x3mm then descaled by brushing with a wire brush. They were cleaned and dried with acetone, then kept in a desiccators before the experiment. The chemical composition of low carbon steel specimen analyzed is as shown in Appendix 1 table.1 this was carried out at the extraction metallurgy assay laboratories in the University of Johannesburg in South Africa Spectral method.

3.3.2 Area and density of specimen

For use in this work, flat low carbon steel bar was cut into rectangular coupons. The area of the specimens was obtained from the relation:

$$A = 2(xy + yz + xz) \dots\dots\dots 3.1$$

Where A = area of specimen

$$x = \text{breadth of specimen} = 15\text{mm}$$

$$y = \text{length of specimen} = 50\text{mm}$$

$$z = \text{thickness of specimen} = 3\text{mm}$$

Thus,

$$\begin{aligned} A &= 2[(15\text{mm} \times 50\text{mm}) + (50\text{mm} \times 3\text{mm}) + (15\text{mm} \times 3\text{mm})] \\ &= 1890\text{mm}^2 \equiv 18.90\text{cm}^2 \end{aligned}$$

The density of low carbon steel is 7.87g/cm^3 (www.azom.com/article.aspx?).

3.3.3 Preparation of Acacia plant extracts

The Acacia Nilotica plant (leaves,seed,pods,bark and seed) were obtained from Nigerian institute of leather and science technology(NILEST) cut into pieces and dried to remove the moisture content.They were then grounded to powder and weighed on the analytical mass balance to 700g according to the method of Loto et al,(2011)

A Soxhlet apparatus (available at NILEST zaria) was used for the extraction. The soxhlet extractor consists of a main extractor and a reflux condenser.The powdered samples were placed in a thimble made of a paper and inserted into a wide central tube of the extractor, solvent (methanol) was placed in the flask and boiled,its vapour passing up the large right hand tube onto the central space above the sample and thence to the the condenser, the condensate then drops back into the raw material through which it percolates leaching solute in the process. When sufficient quantity of the solution has been collected to raise its level to

that of the top of the siphon tubes, the whole of the percolates siphons lower into the flask. The suction effect of the siphoning assist permeation of solvent through the raw materials. A limited amount of hot solvent was thus made to percolate repeatedly through the raw material, the solute from which was transferred to the flask until the required extract quantity was obtained. Plate IV shows a Soxhlet extractor

It is worthy of note here that part per million (ppm) is a term used in chemistry to denote a very, very low concentration of a solution. The inhibitors concentration in ppm was obtained using the relationship (dealloyed.50megs.com).

$$1 \text{ ppm} = 1 \text{ mg/l}$$

For 0.2g inhibitor concentration in 350ml acid solution, we know that 1g = 1000mg

Therefore 0.04g = 40mg. Similarly, 1000ml = 1 liter therefore 100ml = 0.1 liters.

$$\text{Concentration (ppm)} = \text{mass in milligrams} / \text{volume in liters}$$

$$= (40 \text{ mg}) / (0.1 \text{ L}) = 400 \text{ ppm}$$

The above calculation was repeated for 0.06g, 0.08g and 0.1g in 100 ml crude to obtain 600, 800 and 1000 ppm inhibitor concentrations respectively.



Plate;IV: soxhlet extractor (NILEST Zaria)

3.3.4 Phyto-Chemical Analysis

Phyto-chemical screening is the application of simple chemical tests to detect the presence of accumulated natural products. These are referred to as secondary metabolites and they are responsible for the therapeutic properties of plants (Yawas, 2005). Phyto-chemical analysis for the extracts was carried out in the Department of Pharmacognosy, Ahmadu Bello University Zaria. Table 3.2 is the tabulated procedure for the analysis.

Table 3.2 Phytochemical Tests

1.0 Test for Carbohydrates			
	Test	Observation	Inference
(a)	A few drops of molisch reagent was added to little quantity of extract in a test tube and a small quantity of concentrated sulphuric acid was allowed to run down the side of the test tube.	A lower purple to violet colour at the interface	Indicate the presence of carbohydrate
2.0 Test for Cardiac Glycosides			
	Test	Observation	Inference
	Extract was dissolved in glacia acetic acid containing traces of ferric chloride. The test tube was held at angle of 45 degree, 1ml of concentrated sulphuric acid was added down the side	A purple ring colour was formed at interface	Indicates the presence of cardiac glycosides
3.0 Test For Anthraquinones Derivatives			
	Test	Observation	Inference
	Small portion of the extract was shakened with 10ml of benzene and	Pink-red or violet colour is observed	Indicates the presence of free

	filtered. 5ml of 10% of ammonia solution was added to the filtrate and stirred.		Anthraquinones.
4.0 Test for Saponins			
	Test	Observation	Inference
	Small quantity of the extract was dissolved in 10ml of distilled water. This was shaken vigorously for 30 seconds and was allowed to stand for 30 minutes. A honey comb formed for more than 5minutes	A honey comb is formed	Indicates the presence of Saponin.
5.0 Test for Flavonoids			
	Test	Observation	Inference
(a)	Few drops of aqueous NaOH were added to 5ml of extract.	A yellow colouration is observed	Indicates the presence of flavonoid
6.0 Test for Tannins			
	Test	Observation	Inference
(b)	About 0.5ml of extract was dissolved in 10ml of distilled water, then filtrate.	A blue-black precipitate is formed.	Indicate the presence of tannin
7.0 Test for Alkaloids			
	Test	Observation	Inference
(a)	Few drops of mayer's reagent was added to sample of the extract in a test tube.	Cream precipitate is formed	Indicate the presence of alkaloids.
(b)			

(c)	Few drops of dragendorff's reagent was added to the extract		Indicate the presence of alkaloids.
	Few drops of wagner's was added to a small amount of extract.		Indicate the presence of alkaloids.
8.0 Test for Steroid and Triterpenes			
	Test	Observation	Inference
	Equal volume of acetic anhydride was added to the extract. 1ml of concentrated sulphuric acid was added down side the tube.	Red, pink or purple colour was observed and a blue-green or blue was also observed.	Red, pink and purple Indicates the presence of triterpenes and while the blue or blue-green indicates the presence of steroid

3.3.5 Weight Loss Measurements

The specimens were weighed and then fully immersed in each of the test medium contained in a 250ml beaker for 33 days, the test medium was prepared with varying concentration of 400ppm,600ppm 800ppm,1000ppm of each extract and a control medium which was not having any inhibitor according to ASTM G1 (Standard practice for preparing, cleaning and evaluating corrosion test specimen). The specimens were suspended with rubber threads. The specimens (test coupons) was taken out of the test media after the first 5days, then 7

subsequently, the specimen was washed with distilled water, dried with acetone and re-weighed, the weight loss was taken as the difference between the weight of the specimen at a given interval and the initial weight. All these experiments were performed at ambient temperature. Plate V shows the experimental set up



Plate V: Experimental setup.

3.3.6 Effect of Temperature

To ascertain the mechanism of inhibition and to determine the kinetic parameters of the corrosion process, weight loss measurements were performed at 303, 313, 323 and 333K according to (Ndibe et al 2011). In this case, the coupons were retrieved from the solution after 4 hours of immersion instead of 3 hours or less being used in order to magnify the effect of temperature in crude oil which is less corrosive than acid, using the hot water bath. The differences in weight of the coupons were again taken as the weight loss (Yawas, 2005). The rate of corrosion (CR), inhibition efficiency (IE), degree of surface coverage (Θ), film attractive free energy (ΔG_{ads}), activation energy (E_a) and equilibrium constant of adsorption (K_{ads}) were determined using the expressions in section 3.3.6.1-3.3.6.7 below

3.3.6.1 Corrosion Rate

The corrosion rate (C.R) in millimeters penetration per year (mm/y) was calculated, using equation 3.2 (Callister, 1997).

$$C.R = \frac{87.6W}{\rho AT} \dots\dots\dots 3.2$$

Where:

W = weight loss (mg)

A = total surface area of sample

T = time of exposure in hours

ρ = Density of low carbon steel

3.3.6.2 Inhibitor Efficiency

The Inhibitor efficiency (IE) defines the level of performance of inhibitor that causes a decrease in corrosion rate. The inhibitor efficiency (*IE*) was computed using the relationship in equation 3.3 (Khaled, 2008).

$$IE = \frac{(C.R)_0 - (C.R)}{(C.R)_0} \times 100\% \dots\dots\dots 3.3$$

Where: $(C.R)_0$ and $(C.R)$ are the corrosion rates in (mm/y) without and with different concentrations of the inhibitor, respectively.

3.3.6.3 Film Attractive Power

The degree of surface coverage of low carbon steel by molecules of the acacia nilotica inhibitor was calculated by the equation 3.4 (Khaled, 2008).

$$\theta = \frac{(C.R)_0 - (C.R.)}{(C.R)_0} \dots\dots\dots 3.4$$

3.3.6.4 Activation energy (Ea)

Activation energy (Ea) is defined as the minimum energy reacting molecules must possess for a chemical reaction to occur. Activation energy was calculated using the logarithm form of Arrhenius equation below (Nnabuk et al., 2010).

$$\text{Log CR} = \text{Log A} - \frac{E_a}{2.303RT} \dots\dots\dots 3.5$$

Where

E_a the activation energy of the reaction

A Arrhenius pre exponential factor

R Gas constant

CR Corrosion rate

T Absolute temperature

From equation 3.5 the slope of each plot of Log of CR versus 1/T gives its activation energy E_a . (Nnabuk et al., 2010).

3.3.6.5 Adsorption isotherms

In order to study the adsorption characteristics of acacia nilotica juice extracts on low carbon steel surface, calculated values of degree of surface coverage was used to fit curves for Langmuir adsorption isotherms

Langmuir isotherm equation relates the degree of surface coverage (θ) with the concentration of the inhibitor in the bulk electrolyte as follows

$$K_{ads} = \frac{\theta}{c(1-\theta)} \dots\dots\dots 3.6$$

Where:

K_{ads} = Equilibrium constant of adsorption

θ = Degree of surface coverage

C = Concentration of inhibitor

3.3.6.6 Free energy of adsorption

The free energy of adsorption of inhibitors was calculated according to equation 3.7 below (Zhang and Hua, 2009).

$$\Delta G_{ads} = -2.303RT \log(55.5K_{ads}) \dots\dots\dots (3.7)$$

Where:

T = Absolute temperature in Kelvin (K)

R = Universal gas constant (KJ)

ΔG_{ads} = Gibbs energy of adsorption (KJ/mole)

The constant value 55.5 is the concentration of water in solution in mol/l

Enthalpy (ΔH), and entropy (ΔS) of adsorption)

Enthalpy is defined as a measure of the total energy of a thermodynamic system and entropy is the degree of disorderliness. The enthalpy (heat) (ΔH) and the entropy (ΔS) of adsorption of the inhibitors were calculated from transition state equation (Umoren et al., 2008).

$$C.R = \frac{RT}{Nh} \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right) \dots\dots\dots (3.8)$$

Where C.R is corrosion rate, h is plank constant ($6.62606957 \times 10^{-34} m^2 kg/s$), N is the Avogadro's number ($6.02214129 \times 10^{23}$) and R is the gas constant ($0.00831447 KJ/mol$). The values of ΔH and ΔS were obtained from the slope and intercept of $\log \frac{C.R}{T}$ against $1/T$ respectively, with the slope equal $-\Delta H/2.303R$ and intercept equal $\log(R/Nh) + (\Delta S/2.303R)$. (Umoren et al., 2008).

3.4 Microstructure Examination

SEM is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the samples surface topography and composition. The surface morphology of the low carbon steel was studied using a phenom pro X Scanning Electron Microscope (SEM) at the department of chemical Engineering A.B.U Zaria in order to evaluate the surface condition of the metal in contact with Crude oil in the absence and presence of inhibitors.

3.5 Mechanical Properties

3.5.1 Tensile Strength

Tensile strength indicates the ability of a material to withstand forces that pulls it apart as well as the capability of the material to stretch prior to failure. Tensile strength of the materials was carried out at the strength of materials laboratory A.B.U zaria using Denison tensile testing machine of 50tons capacity. The standard specimen were mounted between the upper and lower jaw of the machine to give it a firm grip, load was applied by the means of a load handle at a speed of 2cm/min until the material breaks and the load at that point is recorded

3.5.2 Impact

Impact test were carried out on samples from the 1000ppm medium for all the inhibitor after 33days. The test was carried out using Housfield balance impact machine with 65.079J maximum load of hammer. Each sample was held appropriately in the vice of the impact testing machine and struck with a blow by releasing two pendulums in opposite direction from their calibrated standard height to fracture of the specimen, the energy remaining after fracture was determined in each case from the height rise of the pendulum and their weight, the difference between the energy input and energy remaining represent the energy absorbed by the specimen in that way data were collected from the test.

3.5.3 Hardness

The hardness values of the samples were determined according to the ASTM E140 using the Rockwell hardness tester with a 1/16inch steel ball indenter, minor load of 10KgF, and a major load of 100kgF. Before the test, the mating surface of the indenter, plunger rod and the test samples were thoroughly cleaned by removing the dirt and scratches. The test was carried out

by the indenter moving down into position on the specimensurface,a minor load is applied and a zero reference position is established.A major load is applied for some period then released leaving the minor load,the difference in depth from the zero reference position as a result of the application of the major load gives the Rockwell hardness value.

CHAPTER FOUR

4.0

RESULTS AND DISCUSSION

4.1

RESULTS

Table 4.1 Elemental composition of low carbon steel

C	Si	Mn	P	S	Cr	Mo	Ni	Cu	Al
%	%	%	%	%	%	%	%	%	%
0.215	3.350	1.316	0.102	<0.100	0.029	0.015	0.022	0.012	0.130

As	B	Ca	Co	Mg	N	Nb	Pb	Sn	Ti
%	%	%	%	%	%	%	%	%	%
<0.0050	0.0041	~0.0072	0.0063	0.014	0.653	0.220	<0.100	<0.0020	0.0042

V	W	Zn	Zr	Se	Fe
%	%	%	%	%	%
<0.0050	<0.010	0.013	<0.0020	<0.020	93.65

Table 4. 2: Phytochemical Screening of Extracts

Chemical Constituent	Leaves	Bark	Root	Pod	Seed
Carbohydrates	+	+	+	+	+
Anthraquinone	-	+	-	-	-
Cardiac glycoside	+	+	+	+	+
Saponis	+	+	+	+	+
Steroid	+	+	+	+	+
Triterpene	+	+	+	+	+
Tannins	+	+	+	+	+
Flavonoid	+	+	+	+	+
Alkaloid	+	+	+	+	-

Key

+.....indicate presences

-.....indicate absence

4.1.1 Results obtained from corrosion test.

Figures 4.1-4.32 showed the results obtained from corrosion test using *Acacia nilotica* plant extract as inhibitor in crude oil.

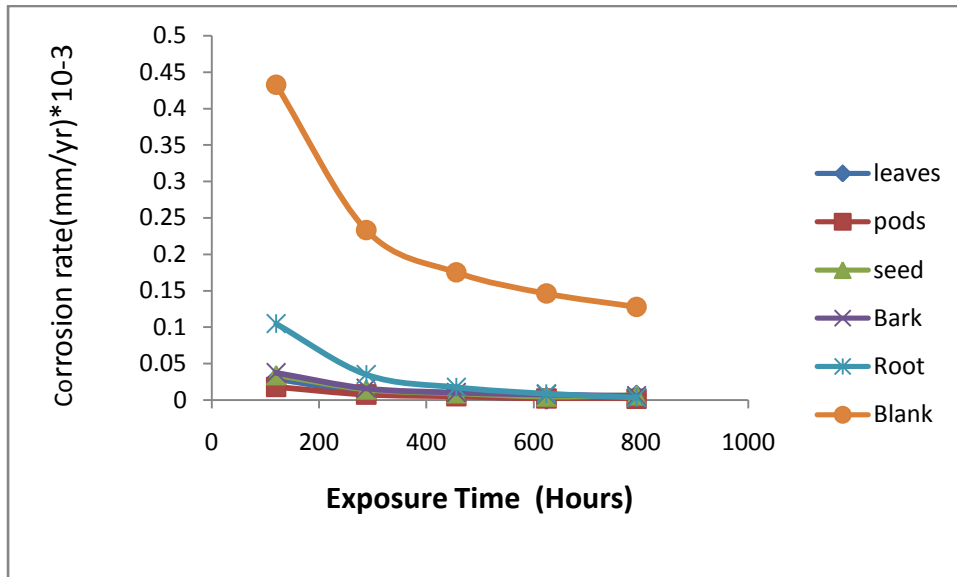


Fig. 4.1: Variation of Corrosion rate with exposure time of low carbon steel in crude oil in blank and presence of 1000ppm concentration of plant extracts.

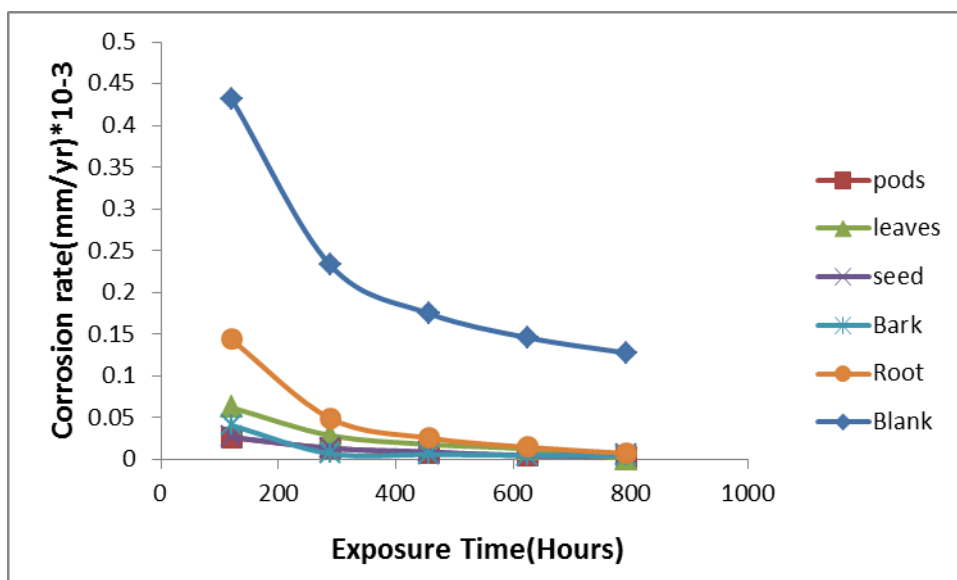


Fig. 4.2: Variation of Corrosion rate with exposure time of low carbon steel in crude oil in blank and presence of 800ppm concentration of plants extracts

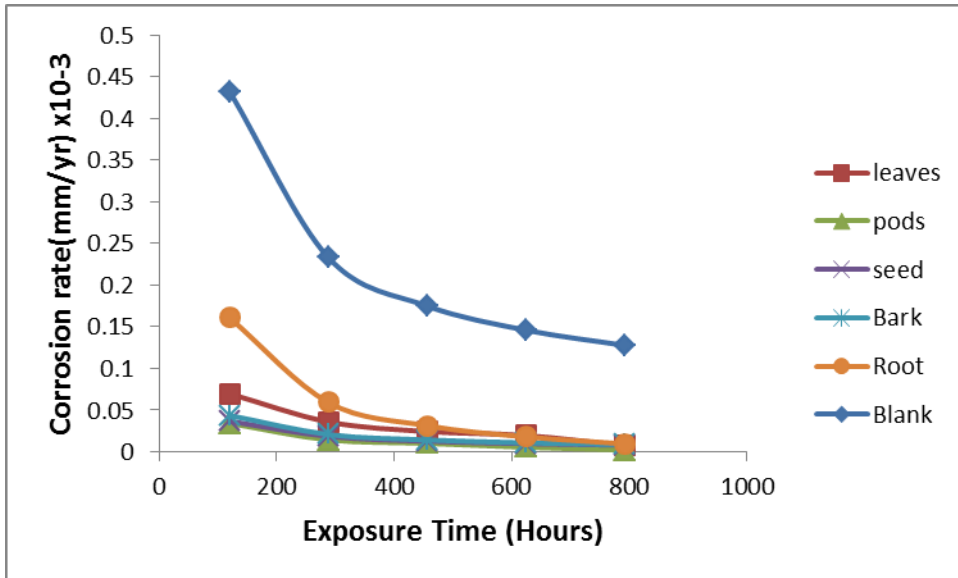


Fig. 4.3: Variation of Corrosion rate with exposure time of low carbon steel in crude oil in blank and presence of 600ppm concentration of extracts.

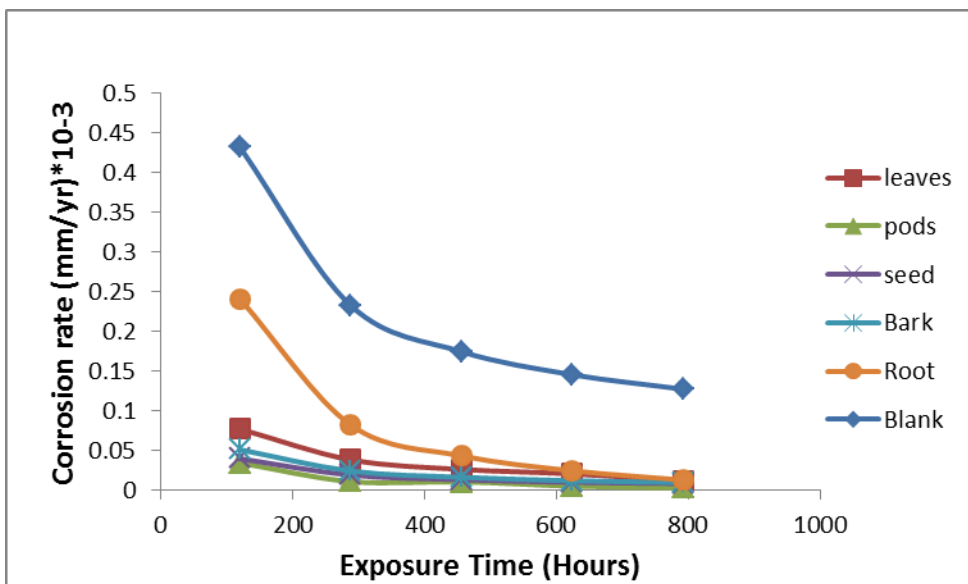


Fig. 4.4: Variation of Corrosion rate with exposure time of low carbon steel in crude oil in blank and presence of 400ppm concentration of extracts.

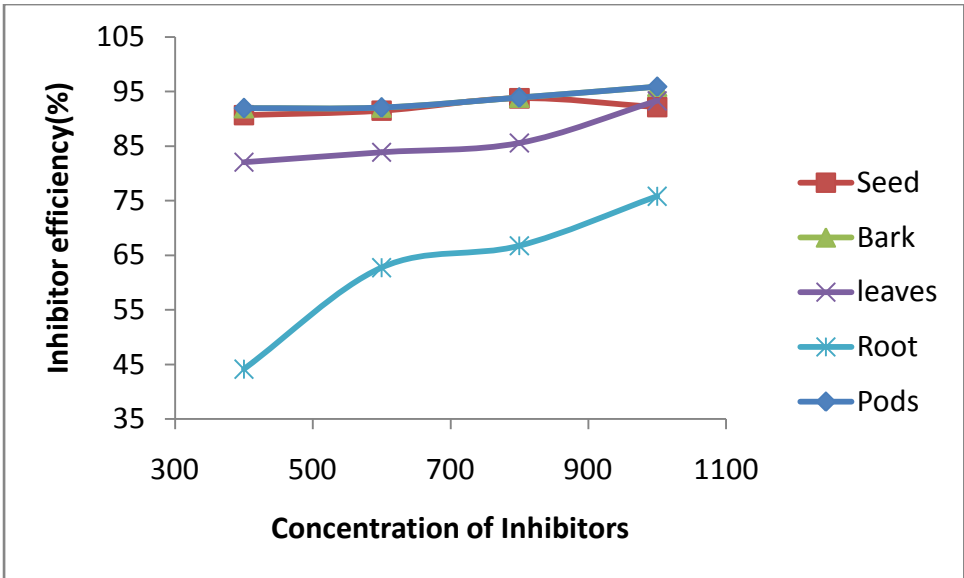


Fig.4.5: Variation of percentage inhibitor Efficiency with inhibitor concentration in crude oil at ambient temperature after 5days

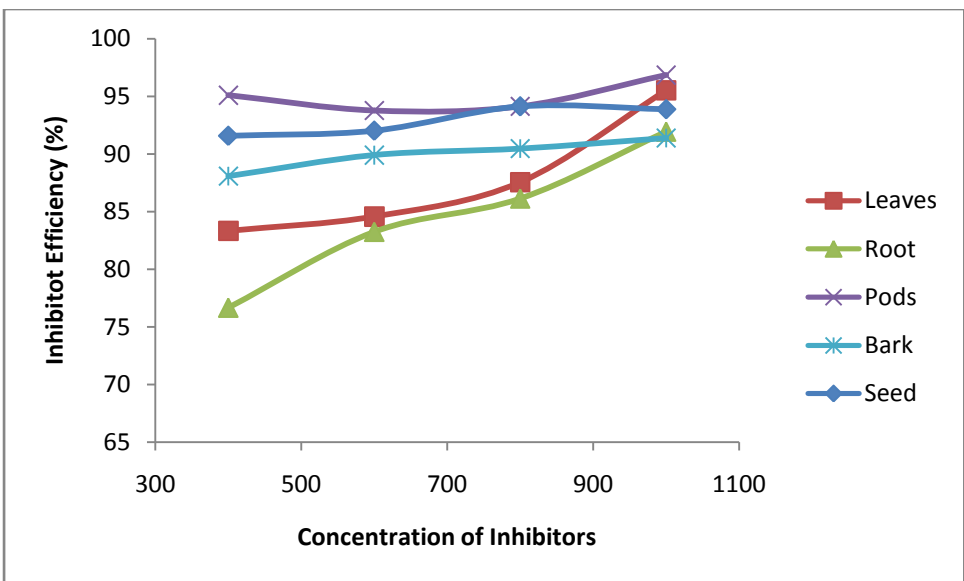


Fig.4.6: Variation of inhibitor Efficiency with inhibitor concentration in crude oil at ambient temperature after 12days

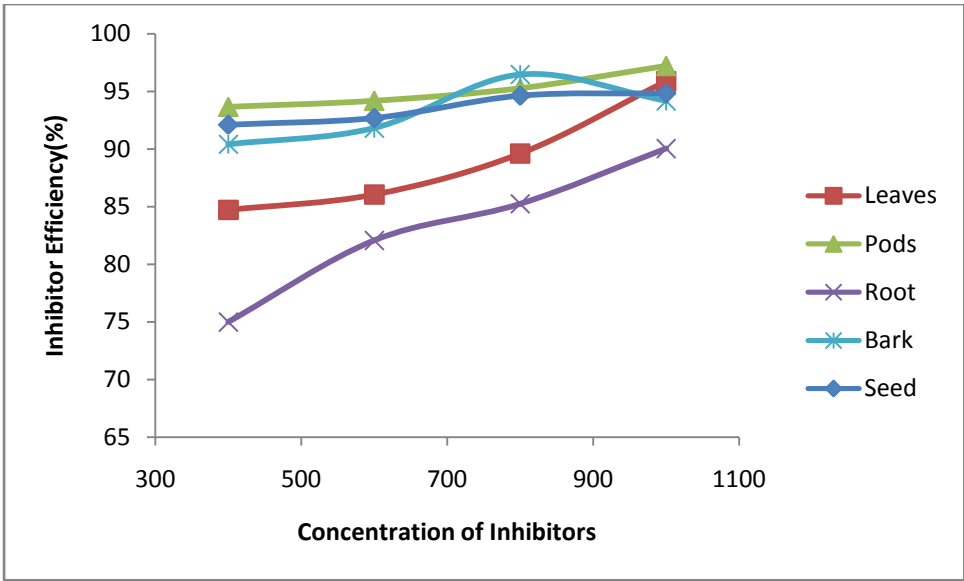


Fig.4.7: Variation of inhibitor Efficiency with inhibitor concentration in crude oil at ambient temperature after 19days

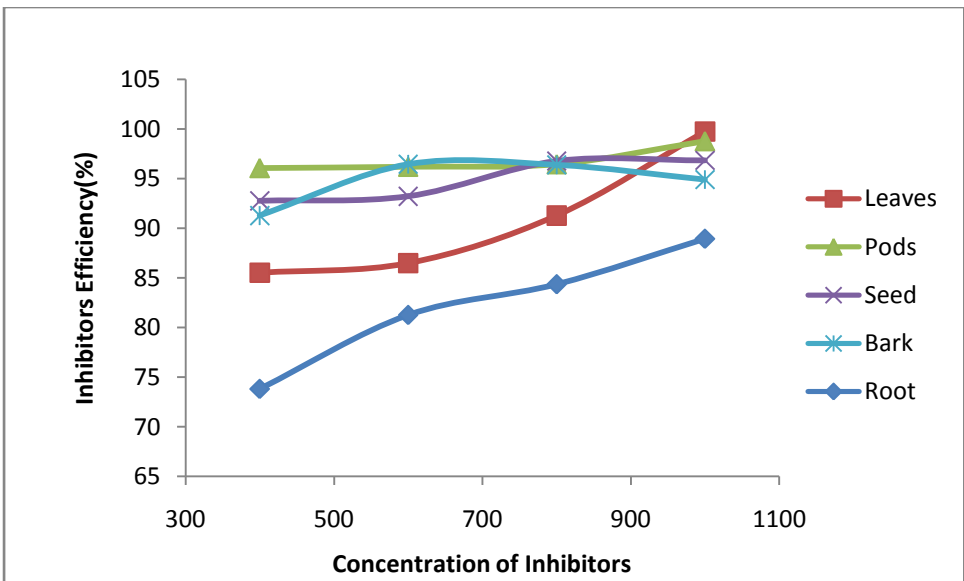


Fig.4.8: Variation of inhibitor Efficiency with inhibitor concentration in crude oil at ambient temperature after 26days

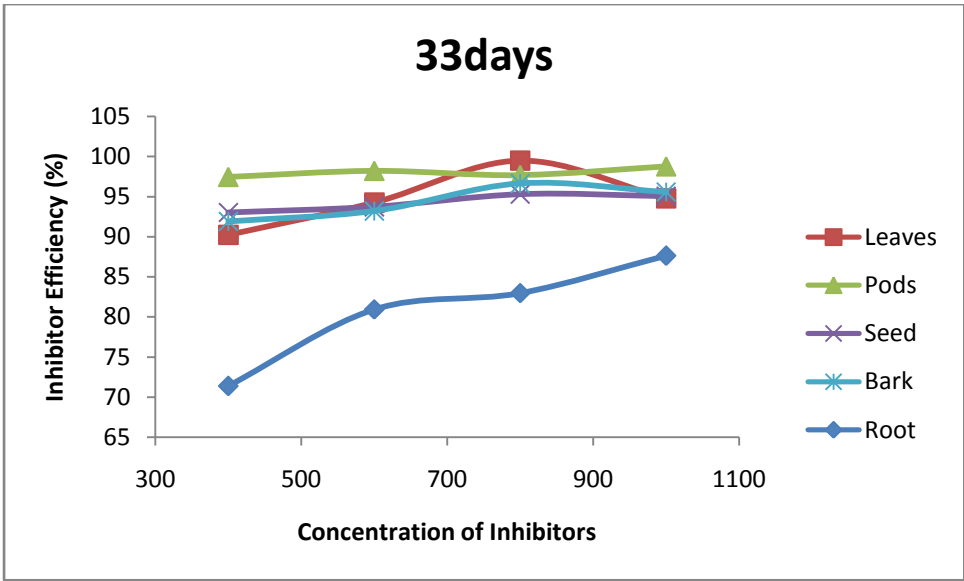


Fig.4.9: Variation of inhibitor Efficiency with inhibitor concentration in crude oil at ambient temperature after 33days.

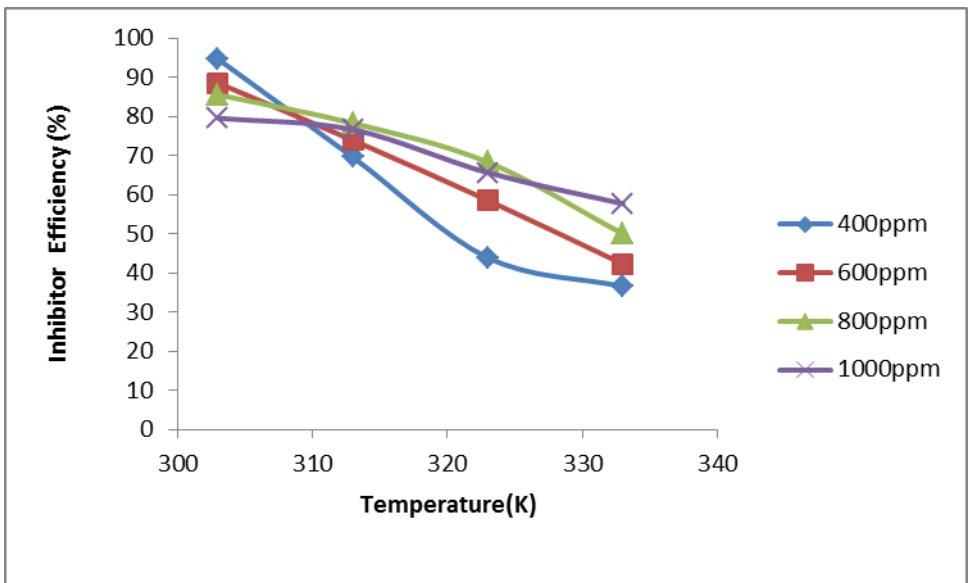


Fig.4.10: Variation of inhibitor Efficiency with temperature for low carbon steel in crude oil in the presence of various concentration of root extract.

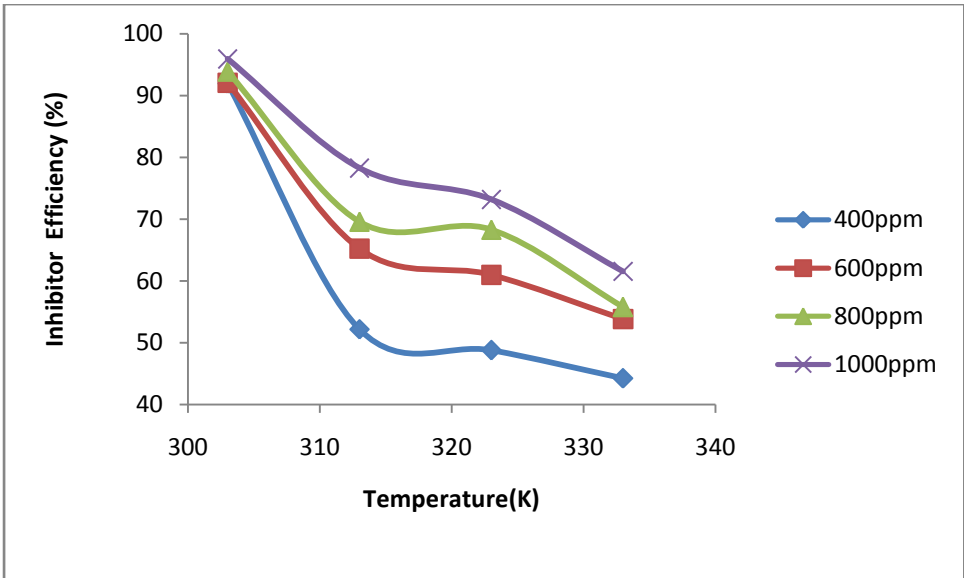


Fig.4.11: Variation of inhibitor Efficiency with temperature for low carbon steel in crude oil in the presence of various concentration of pods extract

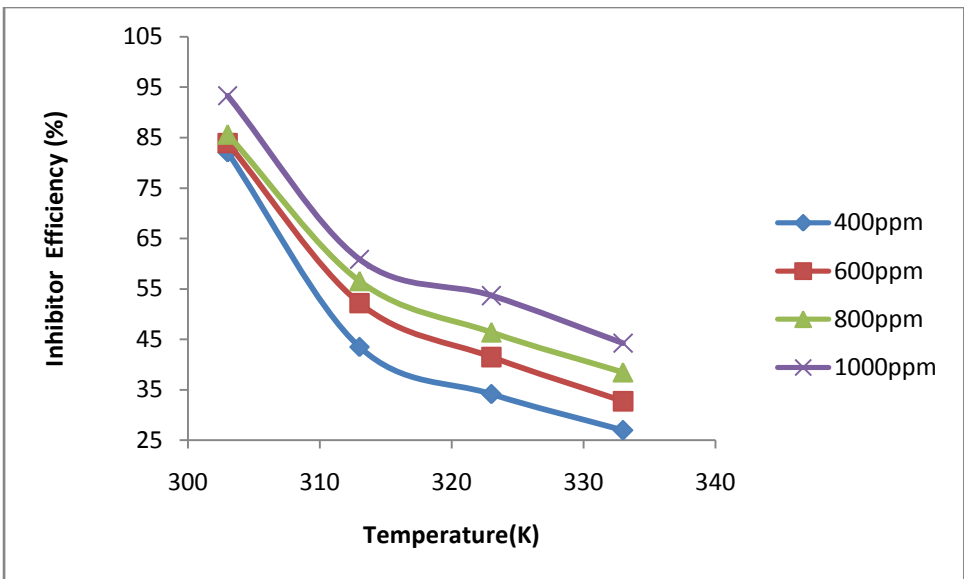


Fig.4.12: Variation of inhibitor Efficiency with temperature for low carbon steel in crude oil in the presence of various concentration of leaves extract.

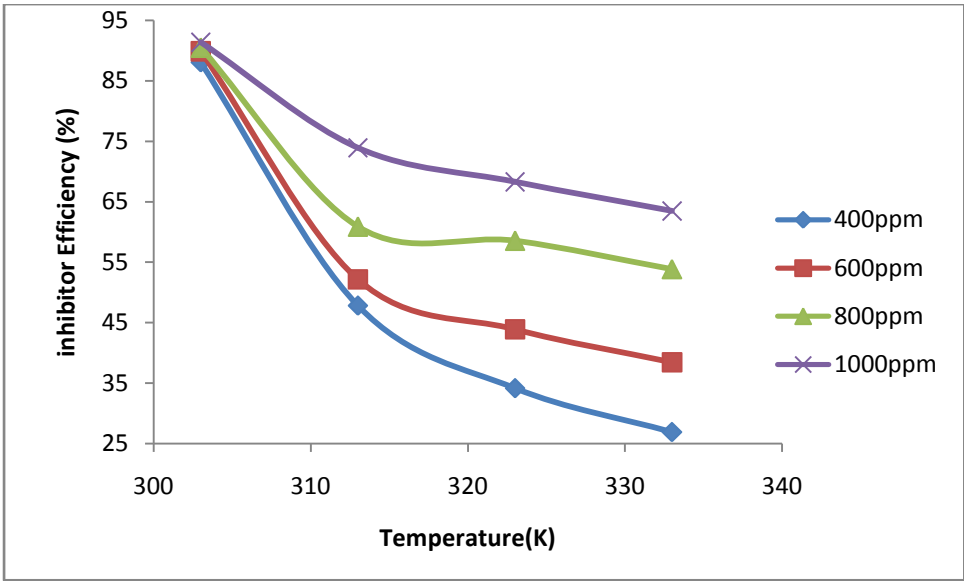


Fig.4.13: Variation of inhibitor Efficiency with temperature for low carbon steel in crude oil in the presence of various concentration of bark extract

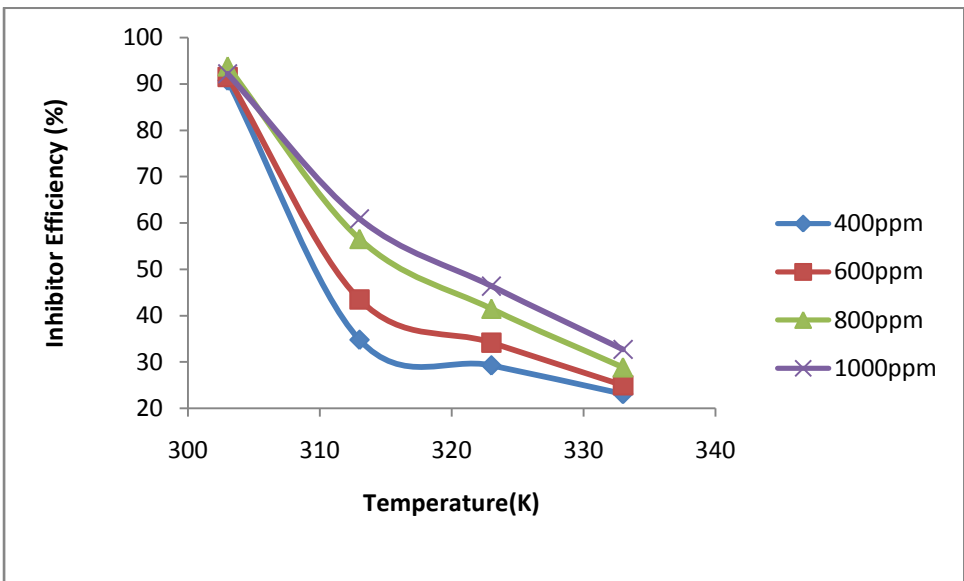


Fig.4.14: Variation of inhibitor Efficiency with temperature for low carbon steel in crude oil in the presence of various concentration of seed extract.

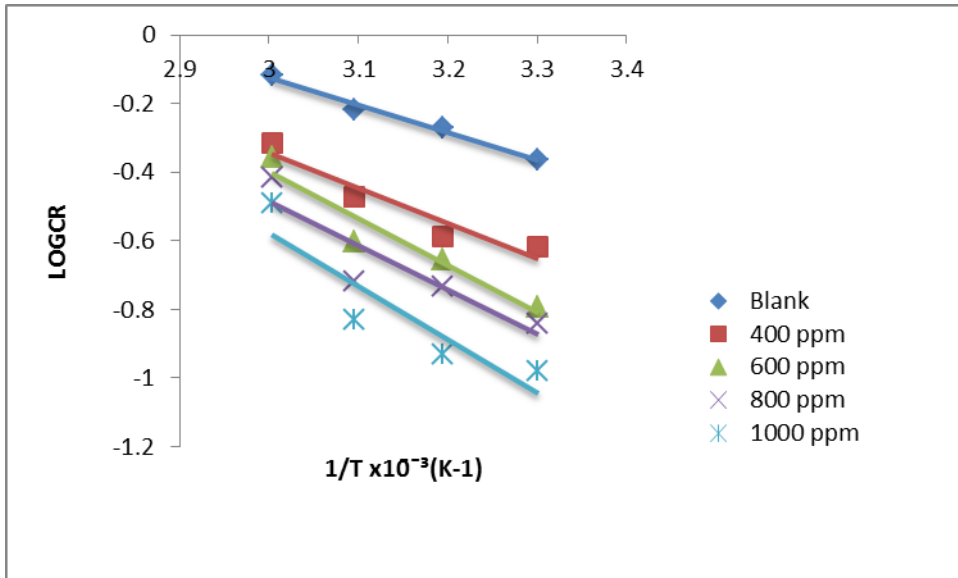


Fig. 4.15: Arrhenius plot for low carbon steel in crude oil in the blank and presence of various concentration of root extract.

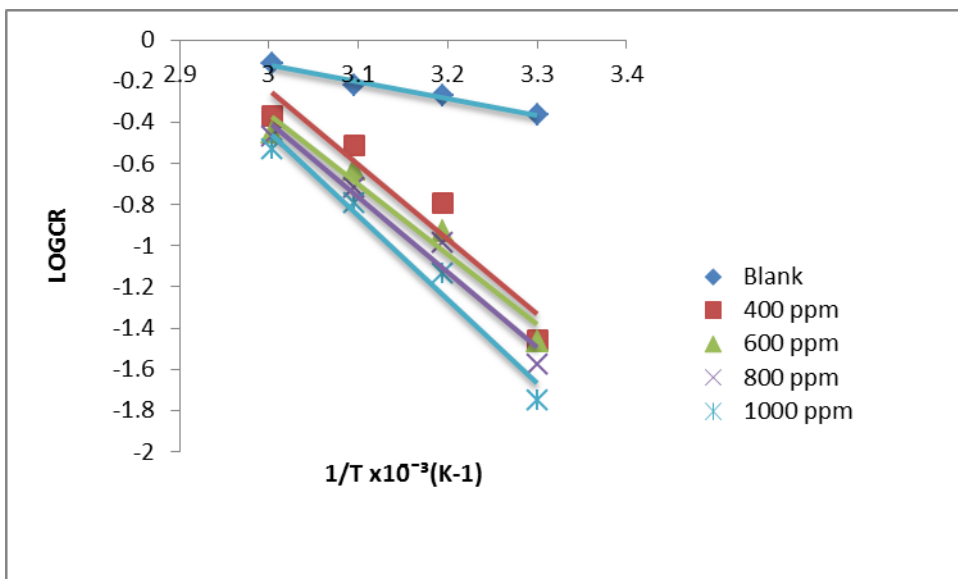


Fig. 4.16: Arrhenius plot for low carbon steel in crude oil in the blank and presence of various concentration of pods extract.

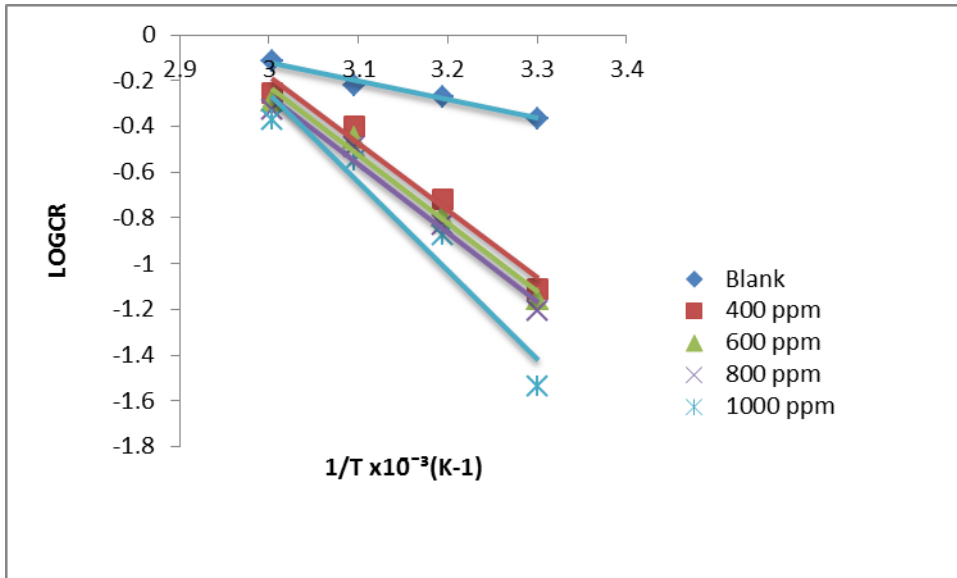


Fig. 4.17: Arrhenius plot for low carbon steel in crude oil in the blank and presence of various concentration of leaves extract.

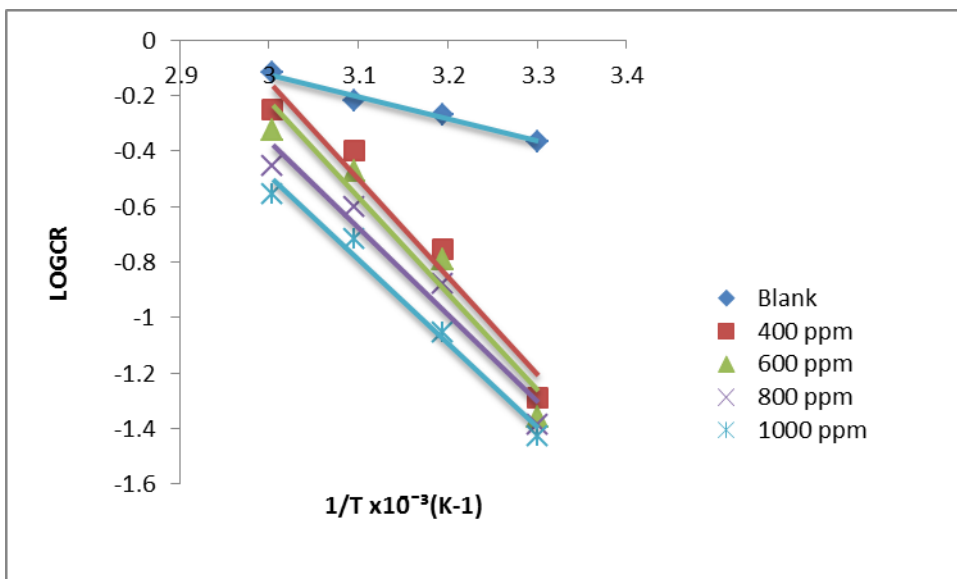


Fig. 4.18: Arrhenius plot for low carbon steel in crude oil in the blank and presence of various concentration of bark extract.

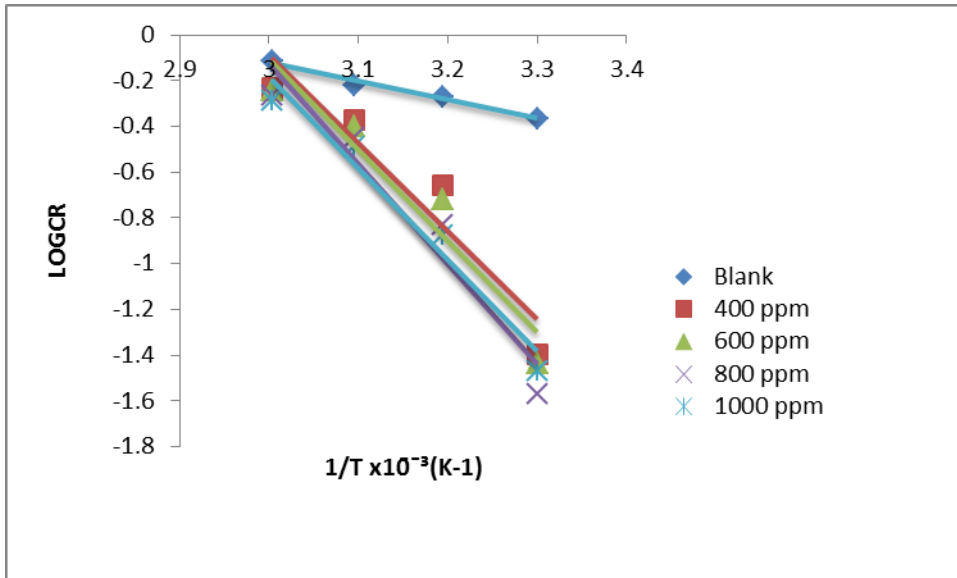


Fig. 4.19: Arrhenius plot for low carbon steel in crude oil in the blank and presence of various concentration of seed extract.

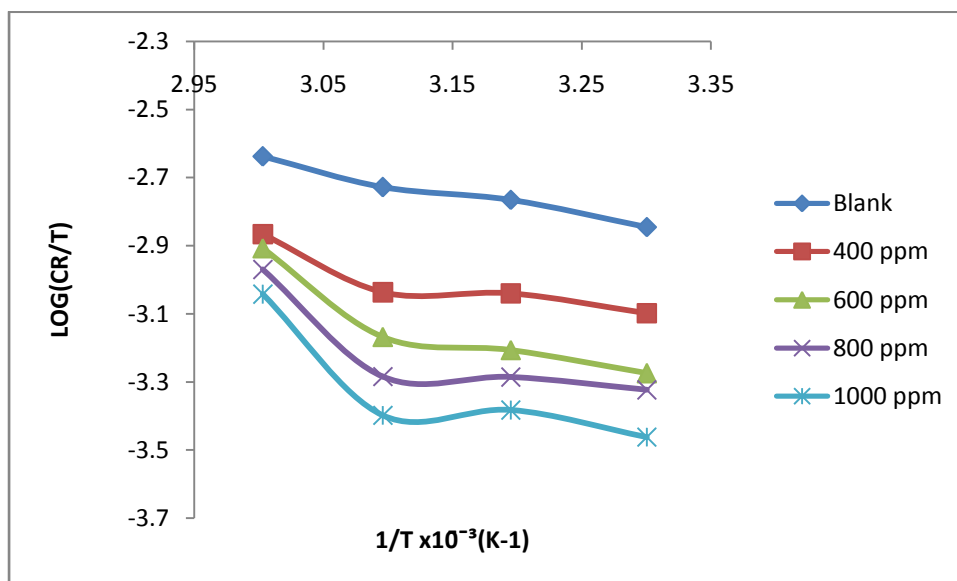


Fig. 4.20: Plot of log (CR/T) against 1/T for the corrosion of low carbon steel in crude oil in the blank and presence of different concentrations of root extract.

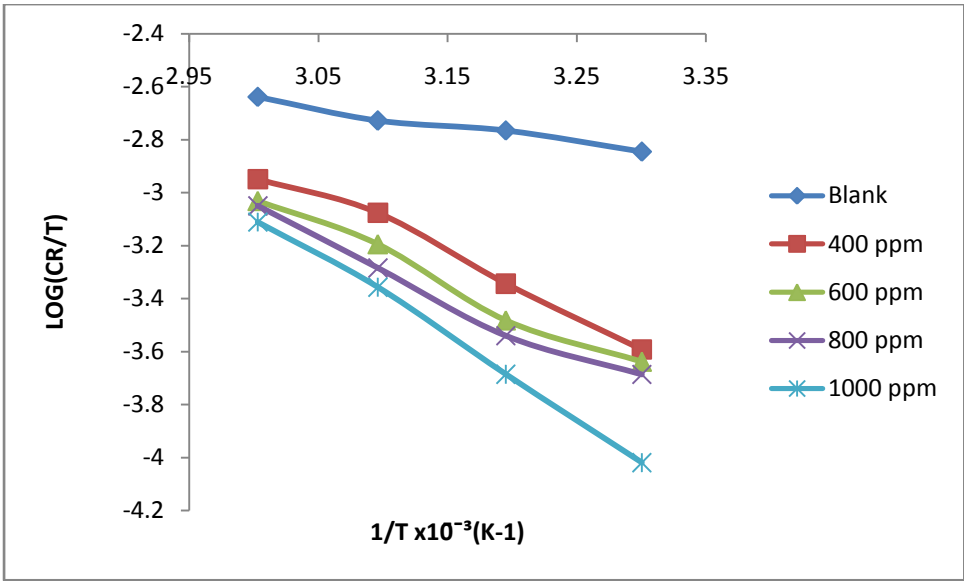


Fig. 4.21: Plot of log (CR/T) against 1/T for the corrosion of low carbon steel in crude oil in the blank and presence of different concentrations of pod extract.

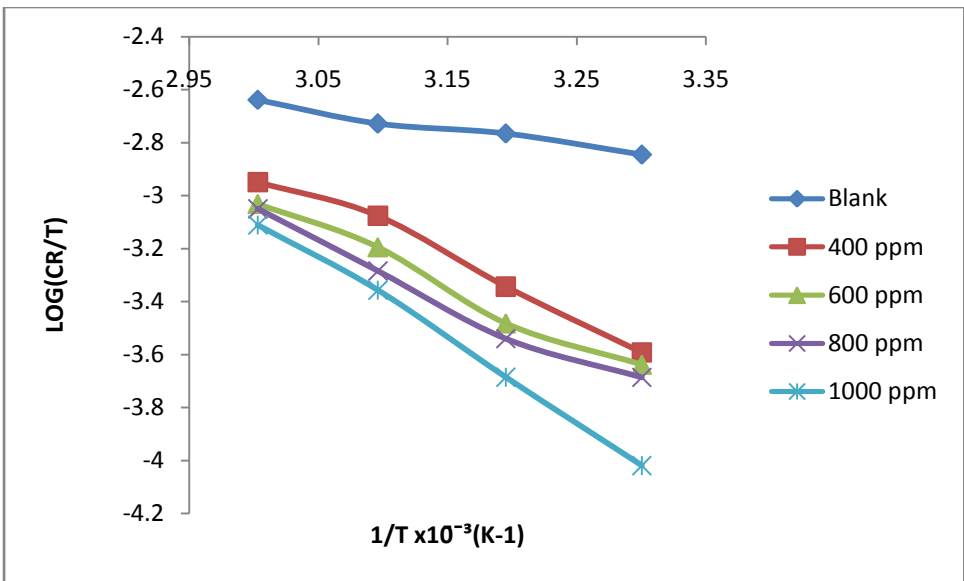


Fig. 4.22: Plot of log (CR/T) against 1/T for the corrosion of low carbon steel in crude oil in the blank and presence of different concentrations of leaves extract.

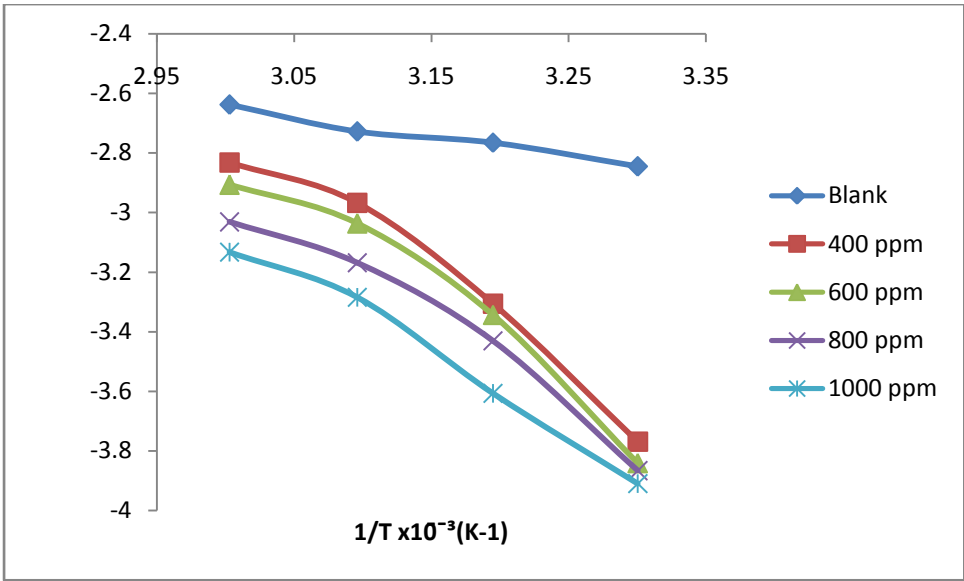


Fig. 4.23: Plot of log (CR/T) against 1/T for the corrosion of low carbon steel in crude oil in the blank and presence of different concentrations of bark extract.

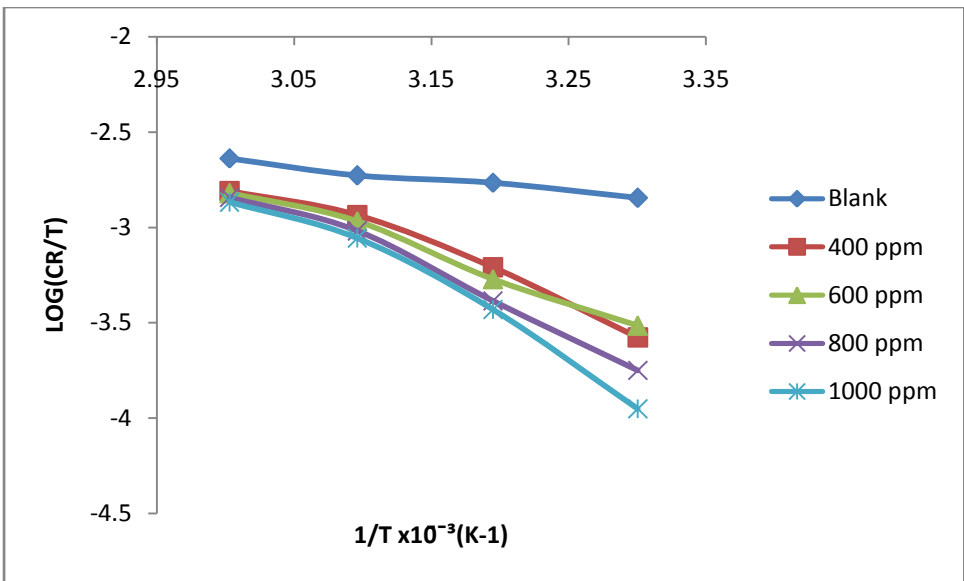


Fig 4.24: Plot of log (CR/T) against 1/T for the corrosion of low carbon steel in crude oil in the blank and presence of different concentrations of seed extract.

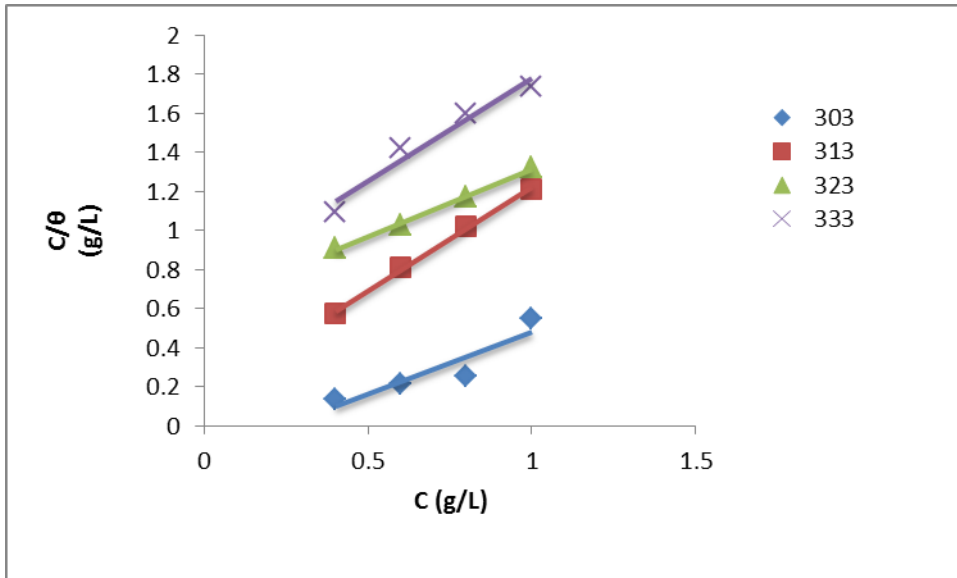


Fig. 4.25: Plot of C/θ against C for corrosion of low carbon steel in crude oil at different concentration of root extract.

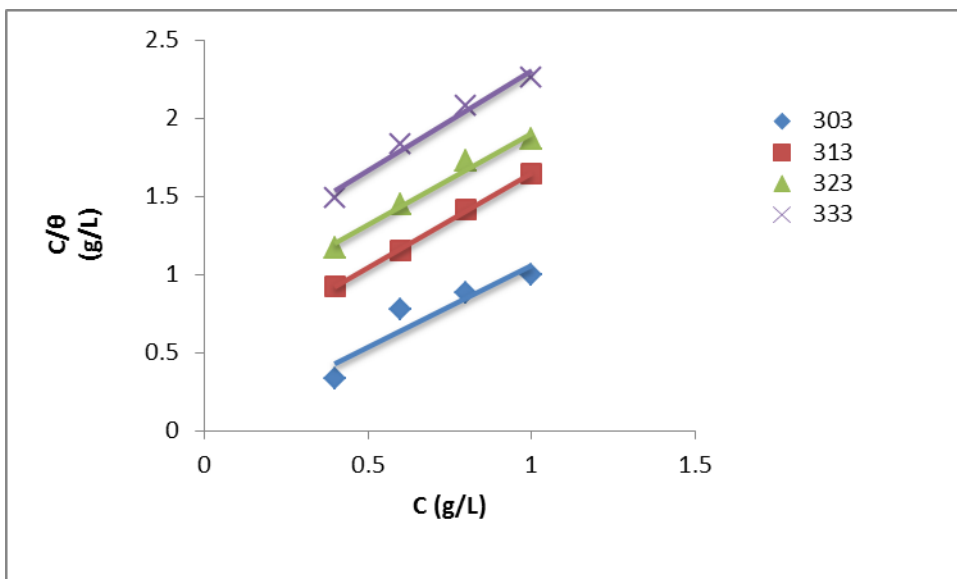


Fig. 4.26: Plot of C/θ against C for corrosion of low carbon steel in crude oil at different concentration of leaves extract.

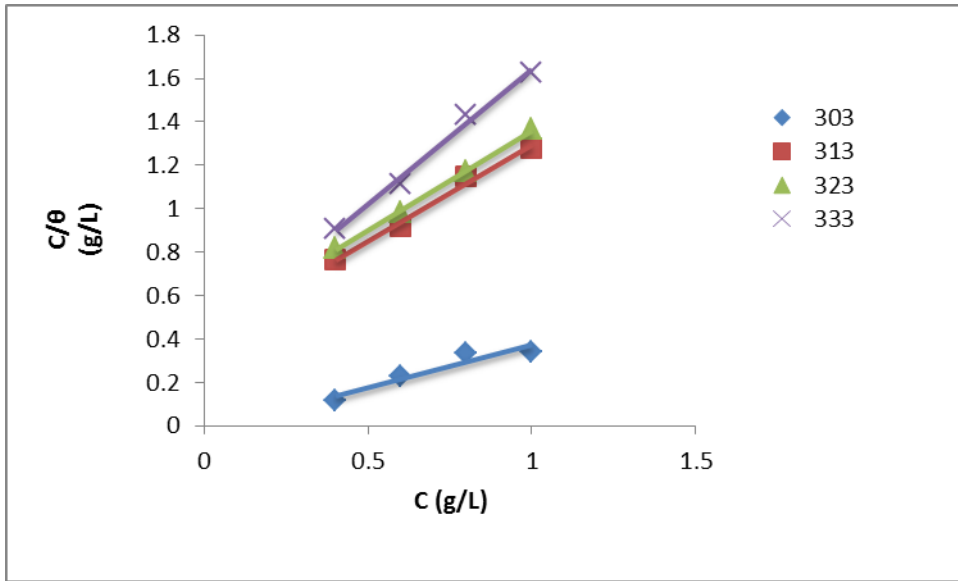


Fig. 4.27: Plot of C/θ against C for corrosion of low carbon steel in crude oil at different concentration of pod extract.

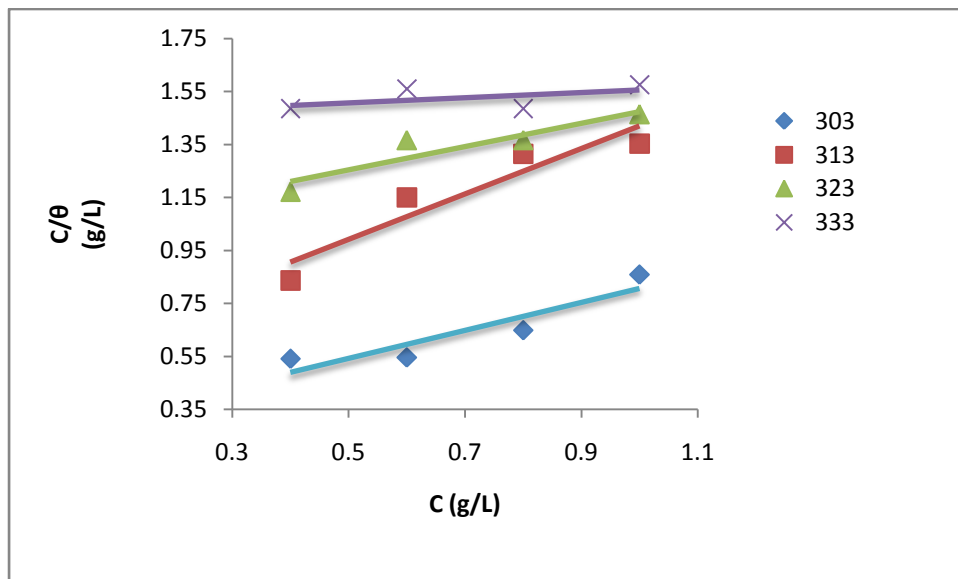


Fig. 4.28: Plot of C/θ against C for corrosion of low carbon steel in crude oil at different concentration of bark extract.

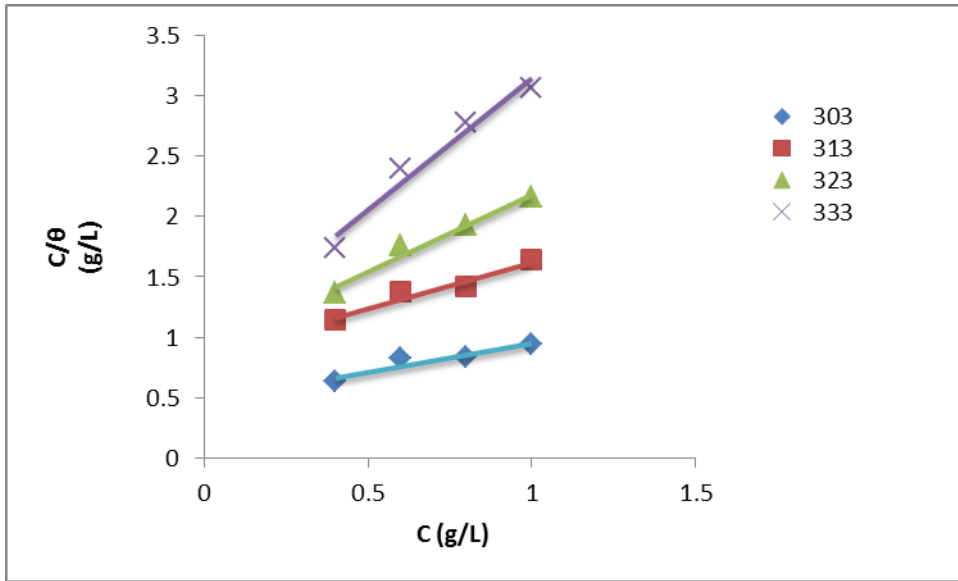


Fig.4.29: Plot of C/θ against C for corrosion of low carbon steel in crude oil at different concentration of seed extract.

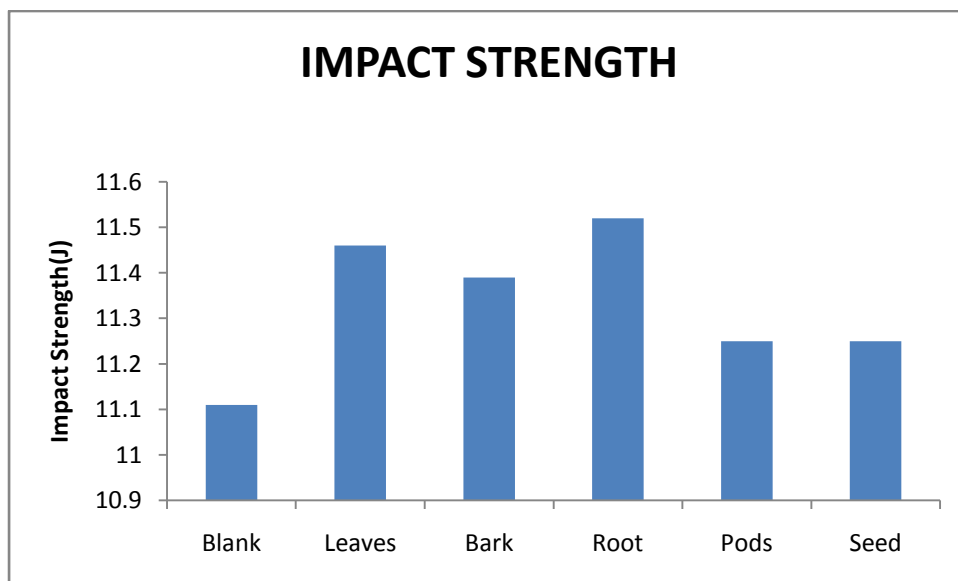


Fig. 4.30: Impact energy for samples from 1000ppm concentration of all the extract after 33days

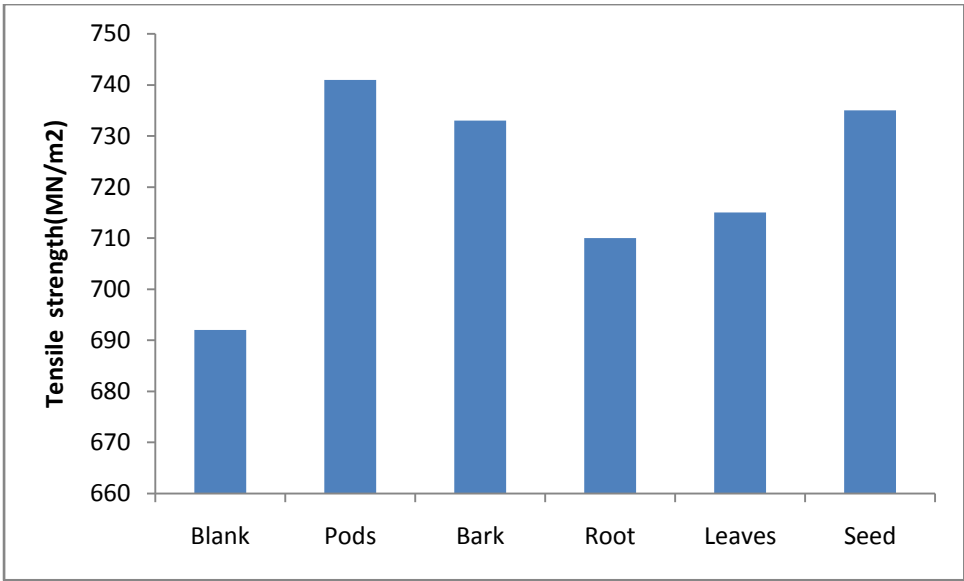


Fig. 4.31: Tensile strength for samples from 1000ppm concentration of all the extract after 33days

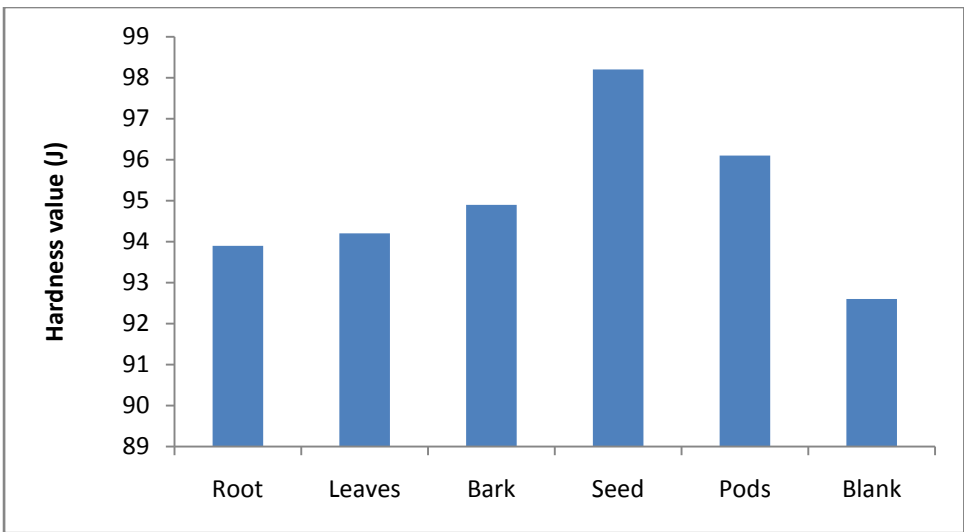


Fig. 4.32: Hardness value for samples from 1000ppm concentration of all the extract after 33day

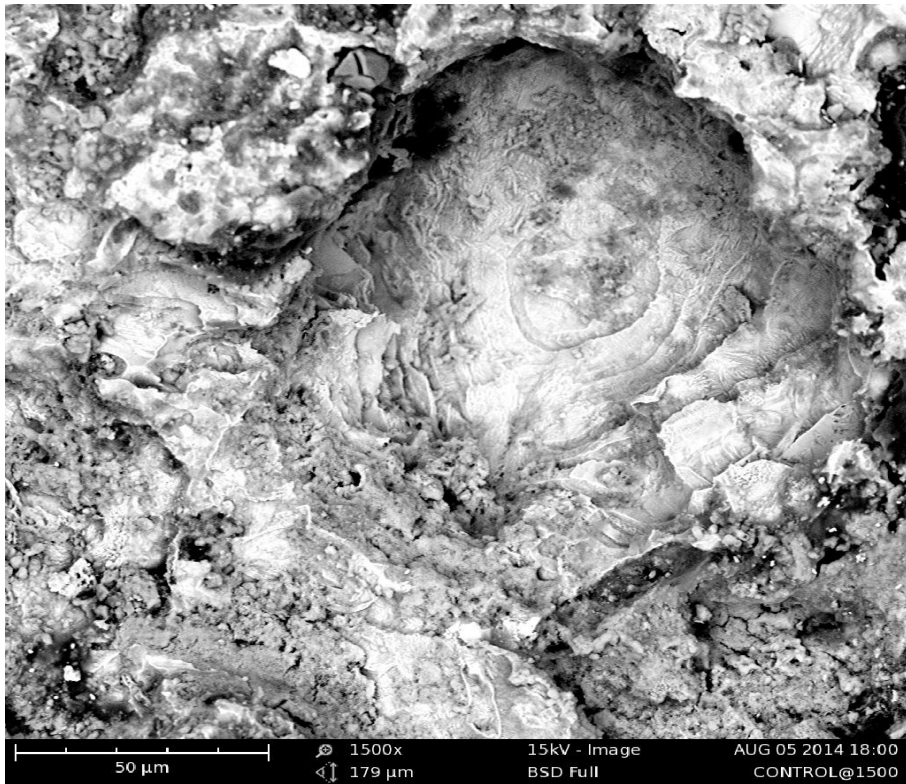


Plate VI: SEM micrograph of low carbon steel in crude oil at 50µm magnification

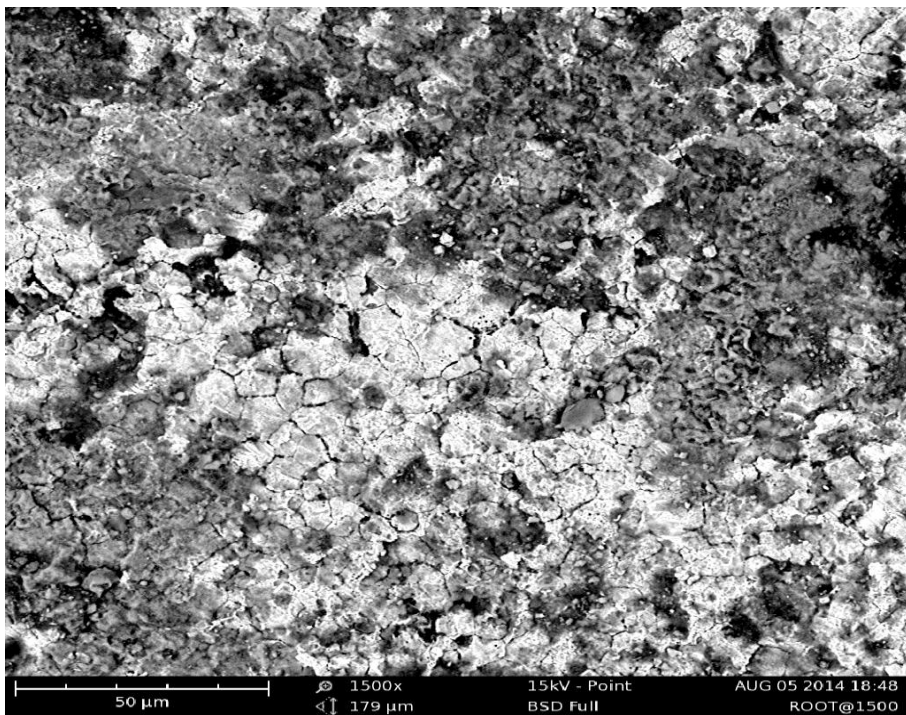
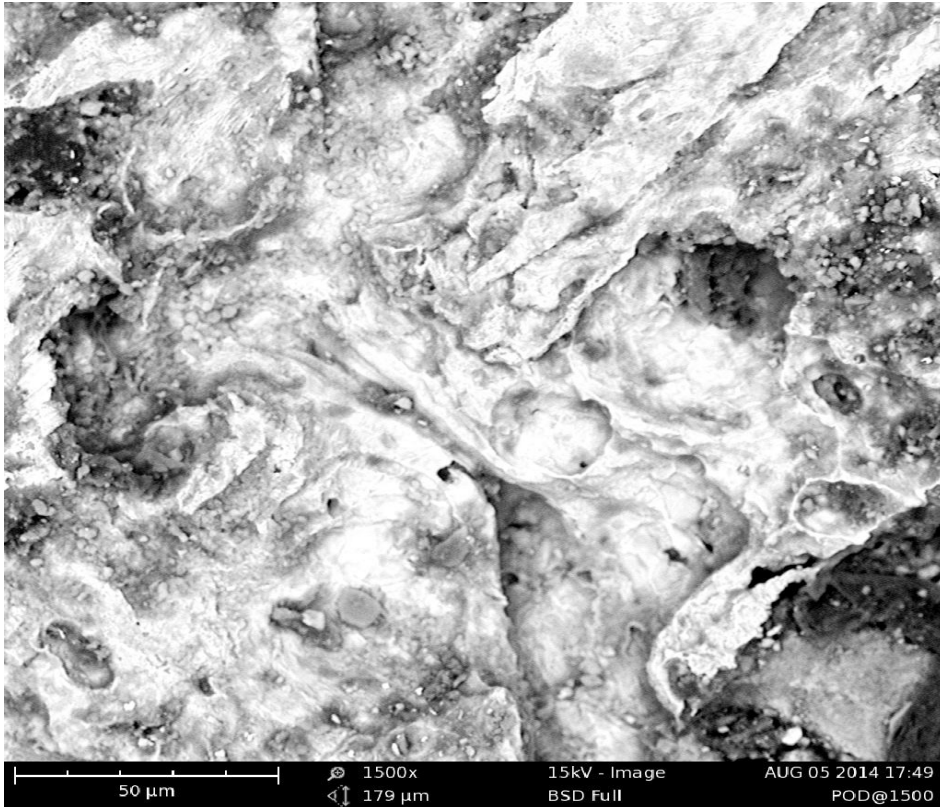


Plate V II. SEM micrograph of low carbon steel in crude oil + 1000ppm of root extract at 50µm magnification



PlateV III: SEM micrograph of low carbon steel in crude oil + 1000ppm of pod extract at 50μm magnification

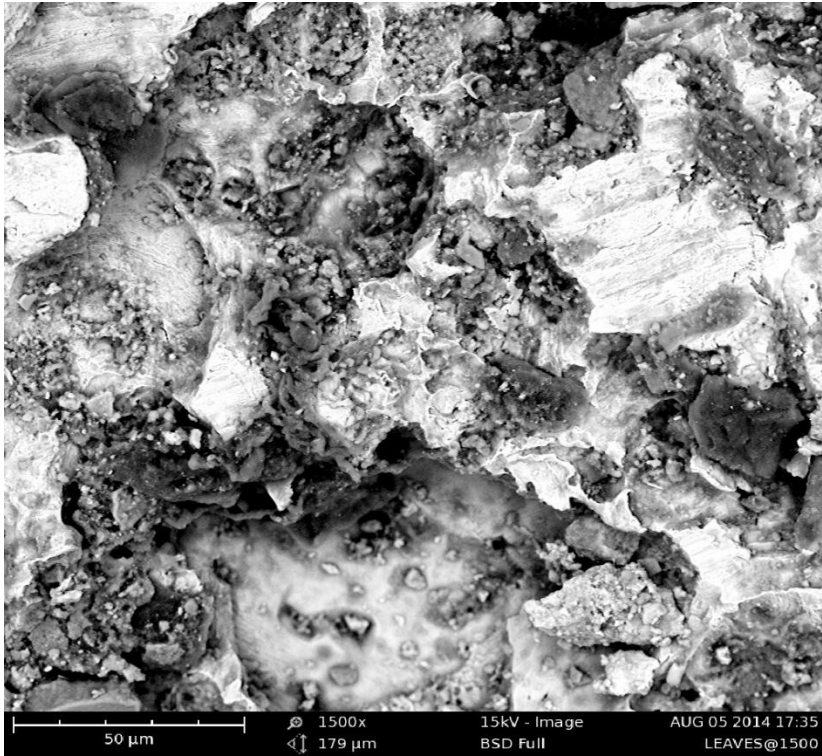
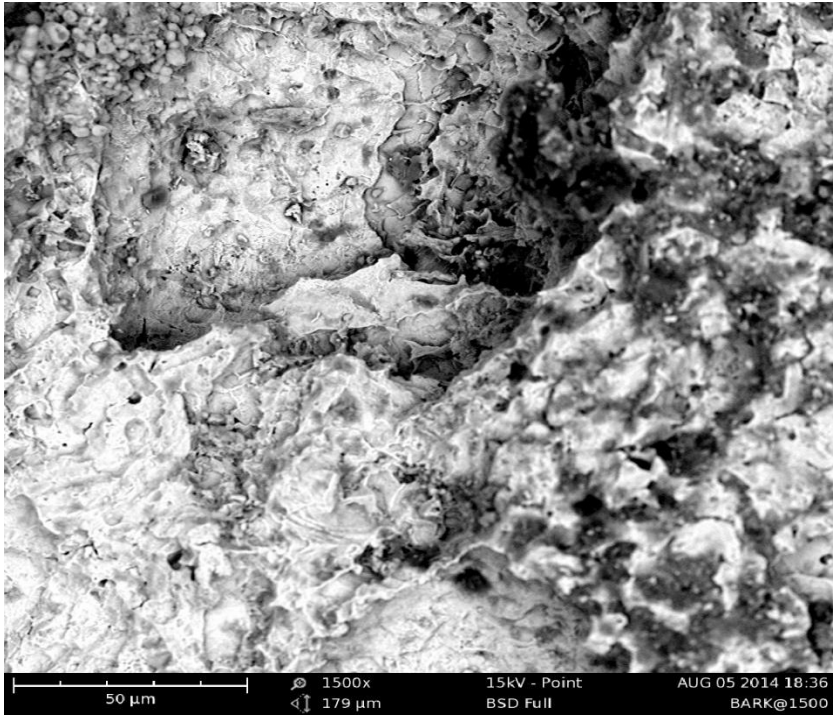


Plate IX: SEM micrograph of low carbon steel in crude oil + 1000ppm of leaf extract at 50µm magnification



PlateX. SEM micrograph of low carbon steel in crude oil + 1000ppm of bark extract

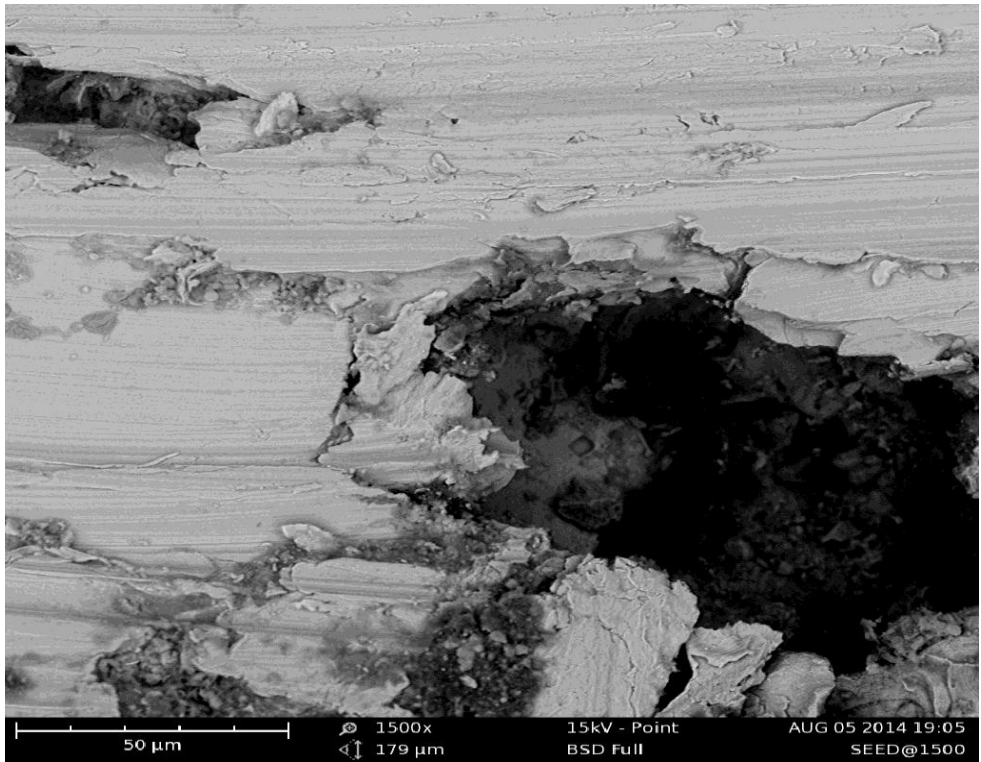


Plate XI: SEM micrograph of low carbon steel in crude oil + 1000ppm of seed extract at 50 μm magnification

4.2

DISCUSSION

4.2.1 Phytochemical Analysis of the Extracts

The phytochemical constituents of methanol extract of *Acacia nilotica* is as shown in Table 4.2. The result obtained indicates that Alkaloids, Cardiac glycosides, saponins, Flavonoids, Tannins, steroid and triterpenes are all present in the leaves, root, pod and bark extracts while the seed extract has Tannins, Cardiac glycosides, saponins, Flavonoids, steroid and triterpenes. The presence of Tannins, an ingredient known to be commonly used for dye, is the most active ingredient in the inhibition of corrosion in steel even though other constituents also have a level of involvement. To inhibit the corrosion of the steel, a thin film is usually formed on the surface of the metal, which then isolates the metal surface from the corrosive environment, causing a reduction in corrosion rate.

4.2.2 Corrosion Rate

Fig 4.1-4.4 showed the effect of inhibitor on the exposure time of low carbon steel in crude oil at concentrations of 400, 600, 800 and 1000 ppm at ambient temperature. The results showed a higher corrosion rate in the uninhibited medium than in the inhibited medium, and this decreased as the days increased from 5 days to 33 days. This behavior is attributed to a high adsorption level by the active ingredient from the plant extract on the metal surface to reduce attack on the metal from the crude oil environment and thereby reducing the weight loss by metal.

4.2.3 Inhibition Efficiency

There seems to be no significant difference in the corrosion rate of the five inhibitors as observed in the graph except for the plot of inhibitor efficiency against concentration that indicates an increase in inhibitor efficiency at higher inhibitor concentration for all the five inhibitors with root having inhibitor efficiency of 94.67%, leaves 95.74%, pods 98.78%, bark 95.58% and seed 96.83 % at the highest concentration of 1000ppm as shown in fig4.5-4.9. The trend of this result is in agreement with works of (Yawas, 2005) and (Kuburi, 2011).

4.2.4 Effect of Temperature

Fig 4.10-4.14 showed the effect of temperature on the inhibitory effect of the inhibitors at various concentrations (400ppm – 1000ppm) at temperatures 313,323 and 333k for a fixed immersion time of 4hours in crude oil. The graph showed that the inhibitor efficiency decrease for all the samples which implies that the rate of corrosion increase with increase in temperature this clearly indicates that the protective films of the inhibitors formed on the surface of the specimen are less stable at higher temperature.

4.2.5 Activation Energy (E_a)

In order to calculate the activation energy (E_a) a graph of CR against the reciprocal of the absolute temperature which slopes is equal to $-E_a/2.303R$ was plotted as shown in figure4.15-4.19. The results obtained for the E_a are shown in Appendix III, Table 24-33, all the values are lower than the threshold value of 80KJ/mol (N.O. Eddy 2009) which supports the mechanism of physical adsorption (physisorption). Higher values of E_a in the presence of inhibitor are a good indication of the extract increasing the energy barrier for the corrosion process.

4.2.6 Enthalpy and Entropy of Adsorption

Figure 4.20 – 4.24 show a plot of $\log CR/T$ against reciprocal of absolute temperature from alternative formulation of Arrhenius equation (transition state equation) which gave a straight line in form of a linear graph with slope equal to $-\Delta H_a/2.303R$ and the intercept equal $[\log(R/Nh)+\Delta S_a/2.303R]$. The enthalpy of activation ($-\Delta H_a$) and the entropy of activation (ΔS_a) were calculated and tabulated in Appendix III, table 29 – 33 for the five inhibitors in the crude oil environment.

The entropy of activation is positive in both absence and presence of inhibitor, the increase in entropy implies disordering took place on going from reactants to the activated complex. The positive sign of enthalpy of activation reflect the endothermic nature of steel dissolution process meaning that dissolution of steel is difficult and it is controlled by activation complex. The increase of E_a and ΔH_a accompanying the increase in the inhibitor concentration is explained by an increase of the energy barrier of the corrosion reaction. The high activation energy in the inhibitors presence further supports the propose physisorption mechanism

4.2.7 Adsorption Mechanism

The Langmuir plotted lines shown in Figure 4.25 – 4.29 is the plots for C/θ against concentration C with the reciprocal of the slope equal to K_{ads} the adsorptive equilibrium constant representing the degree of absorption. The various values of K_{ads} for the five inhibitors are shown in Appendix III, table 29 – 33. The high values of K_{ads} indicate that inhibitors is strongly adsorbed on metal surface.

4.2.8 Free Energy of Adsorption

The Gibbs free energy of adsorption (ΔG_{ads}) was calculated from equation and the results are as shown in Appendix III, table 29 – 33. The negative values of ΔG_{ads} means that the adsorption of the inhibitors on the low carbon steel surface is a spontaneous process and furthermore it also indicates a strong interaction of the inhibitor molecule onto the low carbon steel surface which is in agreement with Zarrouk et al,(2011).

Generally, values of ΔG_{ads} around -20KJ/mol or lower are constant with the electrostatic interaction between the charged molecules and the charged metal (physisorption). Those more negative than -40KJ/mol involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (Chemisorption) as established by Zarrouk et al,(2011).

The calculated values of ΔG_{ads} are greater than -20kJ/mol but less than -40kJ/mol indicating that the adsorption of mechanism of inhibition on low carbon steel by crude oil at the studied temperatures may be combination of both physisorption and chemisorption (Comprehensive adsorption). As posited by Zarrouk et al, (2011).However,physisorption was the major contributor while chemisorption only slightly contributed to the adsorption mechanism judging from the decrease of IE with increase in temperature and the higher values of E_a obtained in the presence of inhibitor when compared to its absence.

4.2.9 Impact Strength, Tensile Strength and Hardness of the Specimens

The mechanical properties (tensile,impact and hardness) of the samples were evaluated after immersion for 33days in the highest concentration of 1000ppm for the five inhibitors.The results obtained as shown in Appendix IV, tables 39-41 shows higher values of tensile(741 MN/m²),impact(11.52J) and hardness(92.6) for the samples from the inhibited medium than the uninhibited medium tensile(692MN/m²),impact(11.11J) and hardness (92.6) which means the ability of the extracts to inhibit corrosion helps maintain the mechanical properties.

4.3 Surface Studies by Scanning Electron Microscopy

Morphological analysis using SEM shows differences in the morphologies of the samples from the inhibited and uninhibited medium. Plate I show the SEM image of specimen immersed in the uninhibited medium for 33days, big pits and cracks observed in the image are due to the effect of corrosion on the specimen, similar images of specimen immersed in the inhibited medium are shown in Plate II-VI. Smother surfaces with little pits and cracks are observed than in the first case this implies corrosion rate was lowered by the extract which is in agreement with the results obtained from the weight loss analysis.

CHAPTER FIVE

5.0

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the results and discussion of this research work the following conclusions are drawn;

1. Acacia nilotica extracts (leaves,pods,seed,bark and root) can successfully serve as corrosion inhibitor for low carbon steel in crude oil based on the efficiency displayed, which the minimum was 56.64% at the lowest concentration of 400ppm.
- 2.The phytochemical analyses show that all the five extract contain tannin and other constituents which were responsible for inhibition of the corrosion in low carbon steel.
3. Protection efficiency of these compounds are seen to increase with increase in inhibitor concentration but decrease with increase in temperature(physisorption) leading to the conclusion that increase in concentration resulted to increase in the protection films on the metal surface as a result of displacement of water molecules from the surface of the metal while increase in temperature resulted to less stability of the films found on the metal surface resulting to less protection from the water molecule.
4. As the inhibitor concentration increased, higher activation energy, enthalpy of activation and entropy of activation were obtained which suggest physical mechanism of adsorption (physisorption).
- 5.Mechanical properties result showed higher values of tensile strength (741MN/m^2), impact (11.52J) and hardness value (98,2HRB) for samples from the inhibited medium than the uninhibited with tensile strength(692MN/m^2), impact(11.11J)and hardness value (92.6HRB) this clearly shows that the inhibitors displayed an effective inhibition against stress corrosion cracking of the material in the medium.

6. The result obtained from morphological images using SEM show clear pits and cracks on the sample from the uninhibited medium due to the effect of corrosion when compared with smoother surface of the sample from inhibited medium

7. Based on the inhibitive efficiency, the compounds tested are ranked as follows: pods > seed > leaves > bark > root.

5.2 Recommendations

1. Constraint in the availability of equipment has subjected this research to weight loss methods however, subsequent investigation can be carried out using A.C impedance and linear polarization methods for comparison.

2. The effects of the extracts on other materials like aluminium at various temperatures could be investigated.

3. Mediums such as H_2SO_4 , HCl etc could be used to characterize the inhibition propensity of these inhibitors

REFERENCES

Anafi, F.O and Obi, A.I.(2004): Corrosion inhibition of low carbon steel in simulated media

- by a methanolic extract of bitter leaf. J. Pure and Applied Sci. Vol.7 (2) pp203-210
- Bargal K, and Bargali, S.S. (2009): *Acacia nilotica*: a multipurpose leguminous plant. *Nature and Science*, 7(4):11-19.
- Beniwal, R.S. Toky, O.P. and Sharma, P.K.(1992): Effect of VA mycorrhizal fungi and phosphorus on growth and nodulation of *Acacia nilotica* (L.) Willd ex Del. *Crop Res.* 5: 172-176.
- Benjamin, D. C. Richard, A. L. and David, H. R (2006). *Corrosion Prevention and Control's Program Management Guide for Selecting Materials*. 2nd Edition: Advanced Materials, Manufacturing, and Testing Information Analysis Center (AMMTIAC), New York.
- Bill, N and Gareth, H, (2003). NPL. *Beginners Guide to Corrosion*, pp. 1-10.
- Brenan, J.P. (1983): *Manual on taxonomy of Acacia species: present taxonomy of four species of Acacia (A. albida, A. senegal, A. nilotica, A. tortilis)*. FAO, Rome: 20-24.
- Callister, W.D. (1997). *Material Science and Engineering* (Fourth Edition ed.). John Wiley and Sons New York.
- Callister, W.D. (2003). *Material Science and Engineering* (Sixth Edition ed.). John Wiley and Sons New York.
- Corrosion Control Solution (n.d.) Retrieved March 12, 2013, from http://www.correx.com/library_corrosion_control_solutions.phyp
- Ernest, W.k. (2001): Use of corrosion inhibitors on Trans Alaska pipeline. *Corrosion control*, oju ewe pp7-9
- Fontana, M.G, (1987). *Corrosion Engineering* (Third Edition ed.). Mc Graw Hill International.
- Gupta, R.K.(1970) Resource survey of gummiferous acacias in western Rajasthan. *Tropical Ecology* 1970, 11, 148-161.

- Gambo, V.A. (2013): Comparative analysis of the aminolysis of PET and sodium dichromate in 1M HCL and H₂SO₄. Msc Seminar Defence, Department of Mechanical Engineering, ABU, Zaria-Nigeria.
- Hany, M. A, Vagif, M. A, Leylufer, I. A and Teyyub, A. I. (2012): Corrosion protection of Steel Pipelines Against carbon IV oxide corrosion. Chemistry Journal, pp 52-63.
- Iman, H, Gohary, A.L., Amaal H.M. (2007): Seed morphology of Acacia in egypt and its taxonomic significance. Int. J. . Agr.& Bio.9(3):435–438.
- Ita, B.I.(2006): Inhibition of the corrosion of low carbon steel in hydrochloric acid by Isatin and Isatin glycine. Bull. Chem. Soc. Ethiop. 20(2) pp253-258
- Iliyasu, I.(2012):The susceptibility of austenitic stainless steel to stress corrosion cracking in some aggressive environment.
- Khan, R, Barira, I, Mohd, A and Shazi, S. (2009): Antimicrobial Activity of Five Herbal Extracts Against Multi Drug Resistant (MDR) Strains of Bacteria and Fungus of Clinical Origin. Molecules., 14(2): 586-597.
- Khaled, K.F. (2008): New synthesized guanidine derivative as a green corrosion for mild steel in acidic solutions. *Int. Journal of ElectrochemScience* (3), 462-475
- Kuburi, L.S. (2011): Effect of flow velocity and exposure time on corrosion inhibition of low carbon steel in crude oil. Msc Seminar Defence, Department of Mechanical Engineering, ABU, Zaria-Nigeria.
- Lopez, D.A., Schreiner, W.H., de Sanchez, S.R., and simison, S.N (2003) The influence of carbon steel microstructure on corrosion layers: an XPS and SEM characterization. *Appl. Surf. Sci.*, 207, pp 69-85
- Loto, T.R, Loto, C.A, Popoola, .I.P.A and Ranyaos, .M,(2012): "Pyrimidine Derivatives as

Environmentally-Friendly Corrosion Inhibitors: A Review." 7(19), 2697-2705.

Mobin. M, Mossarat . P, Alam Khan. M (2011): Inhibition of Mild Steel Corrosion using L-tryptophan and Synergistic Surfactant Additives. Corrosion Research Laboratory, Department of applied chemistry ,Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh, India-202 002 (india)

Mikhailovskii, Y.N., Marshakov, A.I., and petrov, N.A (1997) Monitoring of underground pipeline corrosion condition with sensory instruments. Prot. Met.,33,pp.293-295

Migahed, M. (2005): Corrosion inhibition of steel pipelines in oil fields by N,N-di(poly oxy ethylene) amino propyl lauryl amide. Progress in Organic Coatings, oju ewe pp. 91-98.

Mahgoub, S. On the subspecies of *Acacia nilotica* in the Sudan. Sudan Silva. 1979, 4, 57-62.

N.O.Eddy, S.A.Odoemelam, Resin and pigment Technology, 2009, 38(2), 111.

Ndibe, O.M, Menkiti M.C, Ijomah M.N.C and Onukwuli O.D. Corrosion inhibition of mild steel by acid extract of *vernonia amygdalina* in HCL and HNO₃. Electronic journal of environmental, agricultural and food chemistry, 10(9), 2011:2847-2860.

New, T.R., A Biology of Acacias. Oxford University Press, Melbourne, 1984,153 pp.

Nnabuk, O.E., Ebenso, E.E, and Ibok, U.J. (2010).Adsorption and quantum chemical studies of the inhibitive properties of tetracycline for the corrosion of mild steel in 0.1M H₂SO₄.*J. Argent. Chem. Soc.*, 97(2), 178-194

Physical Properties of low carbon steel (n.d.).Retrieved September 7, 2015, from

<http://www.azom.com/article.aspx?>

Paul, O.A, Ladan,M and Takuma, S, (2012): "Corrosion Inhibition and Adsorption Behaviour for Low carbon steel by *Ficus Glumosa* Gum in H₂SO₄ Solution". African Journal of Pure and Applied Chemistry, 6(7), 100-106.

- Rani, B.E.A, Basu, B.B. J, (2012). "Green Inhibitors for Corrosion Protection of Metals and Alloys: An Overview". *International Journal of Corrosion*.
- Song, F.M., Kirk, D.W., Graydon, J.W., and Cormack D.E (2004) Predicting carbon dioxide corrosion of bare steel under an aqueous boundary layer. *Corrosion*, 60, pp.736-743
- Shaheen Taj, Papavinasam S and Revie R.W. (2006): Development of green inhibitors for oil and gas application. *Corrosion NACEexpo*, (oju ewe pp 1-6).
- Sarkar, K.T. (1991): *Theory and Practice of Leather Manufacture*. 2nd ed. C.L.S. Press. Madras, p. 298.
- Special Issue on Green approaches to corrosion mitigation. *Int. J. Corros*. Available at <http://www.hindawi.com/journals/ijc/si/gacm/2011>
- Thirakul, S. (1984). *Manual of Dendrology*. 2nd ed. Group Poulin, Quebec, Canada p. 4721984; EL Amin, 1990)
- Umoren, S.A., Edouk, U.M. and Oguzie, E.E. (2008): Corrosion inhibition of mild steel in 1M H₂SO₄ by Polyvinyl Pyrrolidone and Synergistic Iodide Additives. *PortugaliaeElectrochimicaActa*.26(6), 533-546.
- Yawas, D.S. (2005): Suitability assessment of some plant extracts and fatty acid vegetable oils as corrosion inhibitors. Ph.D Desentation in the Department of Mechanical Engineering, ABU, Zaria-Nigeria.
- Yoon-Seok and Srdjan (2010): Determining the corrosive potential of Carbon dioxide transport pipeline in high pCO₂-water environments. *International journal of Greenhouse Gas control* 5(2011) 788-797
- Zarrouk, A., Hammmouti, B., Zarrok, H., Al-Deyab, S.S. and Messali, M. (2011): Temperature effect, activation energy and thermodynamic adsorption studies of l-cysteine methy

ester hydrochloride as copper corrosion inhibitor in nitric acid 2M. International journal of Electrochemical science pp 6261-6274

Zhang, Q.B and Hua, .Y.X, (2009). "Corrosion inhibition of mild steel by alkylimidazolium ionic liquids in hydrochloric acid". *Electrochimica Acta*, 54, 1881-1887.

Appendix I

RESULTS OF WEIGHT LOSS ANALYSIS AT AMBIENT TEMPERATURE

Table 3: Corrosion rate of low carbon steel in crude oil in the absence of inhibitor

Exposure Time (Hrs)	Initial Weight(g)	Final Weight(g)	Weight Loss(g)	Corrosion Rate
120	24.7971	24.709	0.0881	0.432377
288	24.7944	24.6804	0.114	0.23312
456	24.8528	24.7173	0.1355	0.175002
624	24.9188	24.7641	0.1547	0.146007
792	24.16	23.9882	0.1718	0.127751

Table 4: Corrosion rate of low carbon steel in crude oil in the presence of 1000ppm concentration root extract.

Exposure Time (Hrs)	Initial Weight(g)	Final Weight(g)	Weight Loss(g)	Corrosion rate (mm/yr)	θ	IE%
120	27.625	27.6203	0.0047	0.104536	0.758229	75.82293
288	27.2089	27.1997	0.0092	0.034968	0.85	85
456	27.2959	27.2824	0.0135	0.017436	0.900369	90.0369
624	27.8898	27.8727	0.0171	0.008683	0.94053	94.05301
792	27.5873	27.566	0.0213	0.003495	0.972643	97.26426

Table 5: Corrosion rate of low carbon steel in crude oil in the presence of 800ppm concentration root extract.

Exposure Time (Hrs)	Initial Weight(g)	Final Weight(g)	Weight Loss(g)	Corrosion Rate (mm/yr)	θ	IE(%)
120	24.2829	24.2536	0.0293	0.143798	0.667423	66.74234
288	24.6481	24.6239	0.0242	0.049487	0.787719	78.77193
456	24.3688	24.3488	0.020	0.02583	0.852399	85.23985
624	24.984	24.9682	0.0158	0.014912	0.897867	89.78668
792	24.1733	24.1632	0.0101	0.00751	0.941211	94.12107

Table 6: Corrosion rate of low carbon steel in crude oil in the presence of 600ppm concentration root extract

Exposure Time (Hrs)	Initial Weight(g)	Final Weight(g)	Weight Loss(g)	Corrosion Rate (mm/yr)	θ	IE(%)
120	24.4483	24.4354	0.0129	0.160976	0.627696	62.76958
288	24.9363	24.9172	0.0191	0.059303	0.745614	74.5614
456	24.7002	24.6759	0.0243	0.031384	0.820664	82.06642
624	24.9714	24.9424	0.029	0.018027	0.876535	87.65352
792	24.4432	24.4104	0.0328	0.009593	0.924913	92.49127

Table 7: Corrosion rate of low carbon steel in crude oil in the presence of 400ppm concentration root extract

Exposure Time (Hrs)	Initial Weight(g)	Final Weight(g)	Weight Loss (g)	Corrosion Rate (mm/yr)	θ	Inhibitor Efficiency (%)
120	27.2354	27.1972	0.0382	0.187478	0.566402	56.64018
288	27.0922	27.0517	0.0405	0.082819	0.644737	64.47368
456	27.1107	27.0768	0.0339	0.043783	0.749815	74.98155
624	27.0049	26.9783	0.0266	0.025105	0.828054	82.80543
792	27.2104	27.1924	0.0180	0.013385	0.895227	89.5227

Table 8: Corrosion rate of low carbon steel in crude oil in the presence of 1000ppm concentration leaves extract

Exposure Time (Hrs)	Initial Weight(g)	Final Weight(g)	Weight Loss (g)	Corrosion Rate (mm/yr)	θ	Inhibitor Efficiency (%)
120	25.4997	25.4938	0.0059	0.028956	0.933031	93.30306
288	25.3837	25.3786	0.0051	0.010429	0.955263	95.52632
456	25.1869	25.1813	0.0056	0.007233	0.958672	95.86716
624	25.6901	25.6897	0.0004	0.000378	0.997414	99.74144
792	25.135	25.126	0.009	0.006692	0.947614	94.76135

Table 9: Corrosion rate of low carbon steel in crude oil in the presence of 800ppm concentration leaves extract

Exposure Time (Hrs)	Initial Weight(g)	Final Weight (g)	Weight Loss (g)	Corrosion Rate (mm/yr)	θ	Inhibitor Efficiency(%)
120	25.7332	25.7205	0.0127	0.062329	0.855846	85.58456
288	25.1971	25.1829	0.0142	0.029038	0.875439	87.54386
456	25.1869	25.1728	0.0141	0.01821	0.895941	89.5941
624	25.2421	25.2286	0.0135	0.012741	0.912734	91.27343
792	25.0293	25.0284	0.0009	0.000669	0.994761	97.47614

Table 10: Corrosion rate of low carbon steel in crude oil in the presence of 600ppm concentration leaves extract

Exposure Time (Hrs)	Initial Weight(g)	Final Weight(g)	Weight Loss(g)	Corrosion Rate (mm/yr)	θ	Inhibitor Efficiency (%)
120	26.402	26.3878	0.0142	0.069691	0.83882	83.88195
288	26.6056	26.588	0.0176	0.03599	0.845614	84.5614
456	26.4443	26.4254	0.0189	0.02441	0.860517	86.05166
624	26.3914	26.3705	0.0209	0.019726	0.8649	86.48998
792	26.69	26.6801	0.0099	0.007362	0.942375	94.23749

Table 11: Corrosion rate of low carbon steel in crude oil in the presence of 400ppm concentration leaves extract

Exposure Time (Hrs)	Initial Weight(g)	Final Weight(g)	Weight Loss (g)	Corrosion Rate (mm/yr)	θ	Inhibitor Efficiency (%)
120	26.0231	26.0073	0.0158	0.077543	0.820658	82.06583
288	26.4268	26.4078	0.019	0.038853	0.833333	83.33333
456	26.6433	26.6226	0.0207	0.026735	0.847232	84.72325
624	26.6014	26.579	0.0224	0.021141	0.855204	85.52036
792	26.5193	26.5025	0.0168	0.012493	0.902212	90.22119

Table 12: Corrosion rate of low carbon steel in crude oil in the presence 1000ppm concentration pods extract

Exposure Time (Hrs)	Initial Weight(g)	Final Weight(g)	Weight Loss (g)	Corrosion Rate (mm/yr)	θ	Inhibitor Efficiency (%)
120	24.577	24.5734	0.0036	0.017668	0.959137	95.91373
288	24.5882	24.5846	0.0036	0.007362	0.968421	96.84211
456	24.4959	24.4921	0.0038	0.004908	0.971956	97.19557
624	24.0324	24.0305	0.0019	0.001793	0.987718	98.77182
792	24.7778	24.7757	0.0021	0.001562	0.987776	98.77765

Table 13: Corrosion rate of low carbon steel in crude oil in the presence of 800ppm concentration pods extract

Exposure Time (Hrs)	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Corrosion Rate (mm/yr)	θ	Inhibitor Efficiency (%)
120	22.9065	22.9011	0.0054	0.026502	0.938706	93.8706
288	22.1459	22.1392	0.0067	0.013701	0.941228	94.12281
456	22.9448	22.9384	0.0064	0.008266	0.952768	95.27675
624	22.213	22.2075	0.0055	0.005191	0.964447	96.44473
792	22.5017	22.4977	0.004	0.002974	0.976717	97.67171

Table 14: Corrosion rate of low carbon steel in crude oil in the presence of 600ppm concentration pods extract

Exposure Time (Hrs)	Initial Weight(g)	Final Weight(g)	Weight Loss(g)	CR (mm/yr)	θ	Inhibitor Efficiency(%)
120	25.923	25.916	0.007	0.034355	0.920545	92.05448
288	25.7699	25.7628	0.0071	0.014519	0.937719	93.77193
456	25.7221	25.7142	0.0079	0.010203	0.941697	94.16974
624	25.8226	25.8167	0.0059	0.005568	0.961862	96.18617
792	25.6361	25.633	0.0031	0.002305	0.981956	98.19558

Table 15: Corrosion rate of low carbon steel in crude oil in the presence of 400ppm concentration pods extract inhibitor

Exposure Time (Hrs)	Initial Weight (g)	Final Weight (g)	Weight Loss (g)	Corrosion Rate (mm/yr)	θ	Inhibitor Efficiency(%)
120	25.684	25.6769	0.0071	0.034845	0.91941	91.94098
288	25.2249	25.2193	0.0056	0.011452	0.950877	95.08772
456	25.3825	25.3739	0.0086	0.011107	0.936531	93.65314
624	25.2534	25.2473	0.0061	0.005757	0.960569	96.05688
792	25.4467	25.4423	0.0044	0.003272	0.974389	97.43888

Table 16: Corrosion rate of low carbon steel in crude oil in the presence of 1000ppm concentration bark extract

Exposure Time (Hrs)	Initial Weight (g)	Final Weight (g)	Weight Loss (g)	Corrosion Rate (mm/yr)	θ	Inhibitor Efficiency (%)
120	23.594	23.5864	0.0076	0.037299	0.913734	91.37344
288	23.3956	23.3878	0.0078	0.01595	0.931579	93.15789
456	23.9664	23.9585	0.0079	0.010203	0.941697	94.16974
624	23.4026	23.3947	0.0079	0.007456	0.948933	94.89334
792	23.3444	23.3368	0.0076	0.005651	0.955763	95.57625

Table 17: Corrosion rate of low carbon steel in crude oil in the presence of 800ppm concentration bark extract

Exposure Time (Hrs)	Initial Weight (g)	Final Weight (g)	Weight Loss (g)	Corrosion Rate (mm/yr)	θ	Inhibitor Efficiency (%)
120	25.5936	25.5852	0.0084	0.041225	0.904654	90.46538
288	25.1167	25.1132	0.0035	0.007157	0.969298	96.92982
456	25.6885	25.6837	0.0048	0.006199	0.964576	96.45756
624	25.5994	25.5938	0.0056	0.005285	0.963801	96.38009
792	25.9545	25.9487	0.0058	0.004313	0.96624	96.62398

Table 18: Corrosion rate of low carbon steel in crude oil in the presence of 600ppm concentration bark extract

Exposure Time (Hrs)	Initial Weight (g)	Final Weight (g)	Weight Loss (g)	Corrosion Rate (mm/yr)	θ	Inhibitor Efficiency (%)
120	23.9484	23.9395	0.0089	0.043679	0.898978	89.89784
288	23.963	23.9528	0.0102	0.020858	0.910526	91.05263
456	23.4636	23.4525	0.0111	0.014336	0.918081	91.80812
624	23.8472	23.8357	0.0115	0.010854	0.925663	92.56626
792	23.2838	23.2721	0.0117	0.0087	0.931898	93.18976

Table 19: Corrosion rate of low carbon steel in crude oil in the presence of 400ppm concentration bark extract

Exposure Time (Hrs)	Initial Weight (g)	Final Weight (g)	Weight Loss (g)	Corrosion Rate (mm/yr)	θ	Inhibitor Efficiency (%)
120	26.8241	26.8136	0.0105	0.051532	0.880817	88.08173
288	26.4809	26.4688	0.0121	0.024743	0.89386	89.38596
456	26.1223	26.1093	0.013	0.01679	0.904059	90.4059
624	26.1699	26.1567	0.0132	0.012458	0.914674	91.46736
792	26.4458	26.4319	0.0139	0.010336	0.919092	91.9092

Table 20: Corrosion rate of low carbon steel in crude oil in the presence of 1000ppm concentration seed extract

Exposure Time(Hrs)	Initial Weight (g)	Final Weight (g)	Weight Loss (g)	Corrosion Rate (mm/yr)	θ	Inhibitor Efficiency(%)
120	25.3651	25.3582	0.0069	0.033864	0.92168	92.16799
288	25.1976	25.1906	0.007	0.014314	0.938596	93.85965
456	25.5663	25.5593	0.007	0.009041	0.948339	94.83395
624	25.8814	25.8765	0.0049	0.004625	0.968326	96.83258
792	25.5085	25.5	0.0085	0.006321	0.950524	95.05239

Table 21: Corrosion rate of low carbon steel in crude oil in the presence of 800ppm concentration seed extract

Exposure Time (Hrs)	Initial Weight (g)	Final Weight (g)	Weight Loss (g)	Corrosion Rate (mm/yr)	θ	Inhibitor Efficiency (%)
120	23.954	23.9485	0.0055	0.026993	0.937571	93.75709
288	24.2645	24.2578	0.0067	0.013701	0.941228	94.12281
456	23.3432	23.3359	0.0073	0.009428	0.946125	94.61255
624	23.9062	23.9012	0.005	0.004719	0.967679	96.76794
792	23.4249	23.4168	0.0081	0.006023	0.952852	95.28522

Table 22: Corrosion rate of low carbon steel in crude oil in the presence of 600ppm concentration seed extract

Exposure Time (Hrs)	Initial Weight (g)	Final Weight (g)	Weight Loss (g)	Corrosion Rate (mm/yr)	θ	Inhibitor Efficiency (%)
120	25.4122	25.4047	0.0075	0.036808	0.914869	91.48695
288	25.4922	25.4831	0.0091	0.018609	0.920175	92.01754
456	25.5127	25.5028	0.0099	0.012786	0.926937	92.69373
624	25.3028	25.2923	0.0105	0.00991	0.932127	93.21267
792	25.4741	25.4633	0.0108	0.008031	0.937136	93.71362

Table 23: Corrosion rate of low carbon steel in crude oil in the presence of 400ppm seed extract

Exposure Time (Hrs)	Initial Weight (g)	Final Weight (g)	Weight Loss (g)	Corrosion Rate (mm/yr)	θ	Inhibitor Efficiency(%)
120	24.8655	24.8573	0.0082	0.040244	0.827368	82.73684
288	24.0343	24.0247	0.0096	0.019631	0.915789	91.57895
456	24.9897	24.979	0.0107	0.013819	0.921033	92.10332
624	24.4245	24.4133	0.0112	0.010571	0.927602	92.76018
792	24.4155	24.4035	0.012	0.008923	0.930151	93.01513

APPENDIX II

Results of Weight loss Analysis at Elevated Temperature

Table 24: Degree of surface coverage (θ) and percentage inhibition efficiency (% IE) of Root in crude oil at 303-313 K, obtained from weight loss measurement after 4hrs.

Temp (k)	Inhib cond	I W (g)	F W (g)	W L (mg)	CR (mm/y)	Θ	IE %	Log CR
303	Blank	24.7971	22.6971	2.1	0.309191	0	0	-0.50977
	400ppm	27.2354	26.3154	0.92	0.135455	0.561905	56.19047	-0.8682
	600ppm	24.4432	23.6432	0.8	0.117787	0.619048	61.90476	-0.9289
	800ppm	24.2829	23.6829	0.6	0.08834	0.714286	71.42857	-1.05384
	1000ppm	27.5873	27.1873	0.4	0.058894	0.809524	80.95238	-1.22993
313	Blank	27.3231	27.3208	2.3	0.338638	0	0	-0.47026
	400ppm	25.2738	25.2731	0.7	0.103064	0.695652	69.56522	-0.98689
	600ppm	24.9362	24.9356	0.6	0.08834	0.73913	73.91304	-1.05384
	800ppm	25.4997	25.4992	0.5	0.073617	0.782609	78.26087	-1.13302
	1000ppm	24.5368	24.5364	0.4	0.058894	0.826087	82.6087	-1.22993
323	Blank	25.5227	25.5186	4.1	0.603659	0	0	-0.21921
	400ppm	26.5859	26.5836	2.3	0.338638	0.439024	43.90244	-0.47026
	600ppm	26.7006	26.6989	1.7	0.250297	0.585366	58.53659	-0.60154
	800ppm	23.2442	23.2429	1.3	0.191404	0.682927	68.29268	-0.71805
	1000ppm	26.2329	26.2319	1	0.147234	0.756098	75.60976	-0.83199
333	Blank	24.7971	24.7919	5.2	0.765616	0	0	-0.11599
	400ppm	25.2986	25.2953	3.3	0.485872	0.365385	36.53846	-0.31348
	600ppm	26.5575	26.5545	3	0.441701	0.423077	42.30769	-0.35487
	800ppm	23.1214	23.1188	2.6	0.382808	0.5	50	-0.41702
	1000ppm	26.2546	26.2524	2.2	0.323914	0.576923	57.69231	-0.48957

Key

IW = Initial weight

FW = Final weight

WL = Weight loss

CR = Corrosion rate

Θ = surface coverage

IE = Inhibitor Efficiency

Table 25: Degree of surface coverage (θ) and percentage inhibition efficiency (% IE) of Pods in Crude oil at 303-313 K, obtained from weight loss measurement after 4hrs.

Temp(k)	Inhib conc	IW(g)	FW(g)	WL(mg)	CR(mm/yr)	Θ	IE%	Log CR
303	Blank	24.7971	22.6971	2.1	0.309191	0	0	-0.50977
	400ppm	25.684	24.584	1.1	0.161957	0.47619	47.61904	-0.7906
	600ppm	25.923	24.923	1	0.147234	0.523809	52.38095	-0.83199
	800ppm	22.9065	22.3665	0.54	0.079506	0.742857	74.28571	-1.0996
	1000ppm	24.577	23.977	0.6	0.08834	0.714286	71.42857	-1.05384
313	Blank	27.3231	27.3208	2.3	0.338638	0	0	-0.47026
	400ppm	25.5903	25.5892	1.1	0.161957	0.521739	52.17391	-0.7906
	600ppm	23.636	23.6352	0.8	0.117787	0.652174	65.21739	-0.9289
	800ppm	25.0959	25.0952	0.7	0.103064	0.695652	69.56522	-0.98689
	1000ppm	25.1918	25.1913	0.5	0.073617	0.782609	78.26087	-1.13302
323	Blank	25.5227	25.5186	4.1	0.603659	0	0	-0.21921
	400ppm	24.868	24.8659	2.1	0.309191	0.487805	48.78049	-0.50977
	600ppm	23.8393	23.8377	1.6	0.235574	0.609756	60.97561	-0.62787
	800ppm	25.0255	25.0242	1.3	0.191404	0.682927	68.29268	-0.71805
	1000ppm	25.8999	25.8988	1.1	0.161957	0.731707	73.17073	-0.7906
333	Blank	24.7971	24.7919	5.2	0.765616	0	0	-0.11599
	400ppm	25.3276	25.3247	2.9	0.426978	0.442308	44.23077	-0.36959
	600ppm	26.9744	26.972	2.4	0.353361	0.538462	53.84615	-0.45178
	800ppm	25.2576	25.2553	2.3	0.338638	0.557692	55.76923	-0.47026
	1000ppm	25.2188	25.2168	2	0.294468	0.615385	61.53846	-0.53096

Key

IW = Initial weight

FW = Final weight

WL = Weight loss

CR = Corrosion rate

Θ = surface coverage

IE = Inhibitor Efficiency

Table 26: Degree of surface coverage (θ) and percentage inhibition efficiency (% IE) of Leaves in Crude oil at 303-313 K, obtained from weight loss measurement after 4hrs.

Temp(K)	Inhibconcn	IW(g)	FW(g)	WL(mg)	CR(mm/yr)	Θ	IE%	LogCR
303	Blank	24.7971	22.6971	2.1	0.309191	0	0	-0.50977
	400ppm	26.0231	24.7131	1.31	0.192876	0.37619	37.61904	-0.71472
	600ppm	26.402	25.202	1.2	0.176681	0.428571	42.85714	-0.75281
	800ppm	25.7332	25.0332	0.7	0.103064	0.666667	66.66666	-0.98689
	1000ppm	25.4997	24.9097	0.59	0.086868	0.719048	71.90476	-1.06114
313	Blank	27.3231	27.3208	2.3	0.338638	0	0	-0.47026
	400ppm	24.989	24.9877	1.3	0.191404	0.434783	43.47826	-0.71805
	600ppm	25.2701	25.269	1.1	0.161957	0.521739	52.17391	-0.7906
	800ppm	26.2413	26.2403	1	0.147234	0.565217	56.52174	-0.83199
	1000ppm	25.3275	25.3266	0.9	0.13251	0.608696	60.86957	-0.87775
323	Blank	25.5227	25.5186	4.1	0.603659	0	0	-0.21921
	400ppm	26.7803	26.7776	2.7	0.397531	0.341463	34.14634	-0.40063
	600ppm	24.2427	24.2403	2.4	0.353361	0.414634	41.46341	-0.45178
	800ppm	22.3116	22.3094	2.2	0.323914	0.463415	46.34146	-0.48957
	1000ppm	25.261	25.2591	1.9	0.279744	0.536585	53.65854	-0.55324
333	Blank	24.7971	24.7919	5.2	0.765616	0	0	-0.11599
	400ppm	26.7336	26.7298	3.8	0.559489	0.269231	26.92308	-0.25221
	600ppm	22.8208	22.8173	3.5	0.515318	0.326923	32.69231	-0.28792
	800ppm	26.3448	26.3416	3.2	0.471148	0.384615	38.46154	-0.32684
	1000ppm	26.4599	26.457	2.9	0.426978	0.442308	44.23077	-0.36959

Key

IW = Initial weight

FW = Final weight

WL = Weight loss

CR = Corrosion rate

Θ = surface coverage

IE = Inhibitor Efficiency

Table 27: Degree of surface coverage (θ) and percentage inhibition efficiency (% IE) of Bark in Crude oil at 303-313 K, obtained from weight loss measurement after 4hrs.

Temp(K)	Inhibconc	IW(g)	FW(g)	WL(mg)	CR(mm/yr)	Θ	IE%	LogCR
303	Blank	24.7971	22.6971	2.1	0.309191	0	0	-0.50977
	400ppm	26.8241	25.3241	1.5	0.220851	0.285714	28.57142	-0.6559
	600ppm	23.9484	22.6484	1.3	0.191404	0.380952	38.09523	-0.71805
	800ppm	25.5936	24.7536	0.84	0.123676	0.6	60	-0.90771
	1000ppm	23.594	22.834	0.76	0.111898	0.638095	63.80952	-0.95118
313	Blank	27.3231	27.3208	2.3	0.338638	0	0	-0.47026
	400ppm	25.1787	25.1775	1.2	0.176681	0.478261	47.82609	-0.75281
	600ppm	25.15	25.1489	1.1	0.161957	0.521739	52.17391	-0.7906
	800ppm	25.2956	25.2947	0.9	0.13251	0.608696	60.86957	-0.87775
	1000ppm	25.2186	25.218	0.6	0.08834	0.73913	73.91304	-1.05384
323	Blank	25.5227	25.5186	4.1	0.603659	0	0	-0.21921
	400ppm	24.4511	24.4484	2.7	0.397531	0.341463	34.14634	-0.40063
	600ppm	25.2023	25.2	2.3	0.338638	0.439024	43.90244	-0.47026
	800ppm	25.0419	25.0402	1.7	0.250297	0.585366	58.53659	-0.60154
	1000ppm	22.3685	22.3672	1.3	0.191404	0.682927	68.29268	-0.71805
333	Blank	24.7971	24.7919	5.2	0.765616	0	0	-0.11599
	400ppm	25.4986	25.4948	3.8	0.559489	0.269231	26.92308	-0.25221
	600ppm	25.7442	25.741	3.2	0.471148	0.384615	38.46154	-0.32684
	800ppm	24.6269	24.6245	2.4	0.353361	0.538462	53.84615	-0.45178
	1000ppm	24.6692	24.6673	1.9	0.279744	0.634615	63.46154	-0.55324

Key

IW = Initial weight

FW = Final weight

WL = Weight loss

CR = Corrosion rate

Θ = surface coverage

IE = Inhibitor Efficiency

Table 28: Degree of surface coverage (θ) and percentage inhibition efficiency (% IE) of Seed in Crude oil at 303-313 K, obtained from weight loss measurement after 4hrs.

Temp(k)	Inhibconc	IW(g)	FW(g)	WL(mg)	CR(mm/yr)	Θ	IE%	LogCR
303	Blank	24.7971	22.6971	2.1	0.309191	0	0	-0.50977
	400ppm	24.8655	23.8655	1	0.147234	0.523809	52.38095	-0.83199
	600ppm	25.4122	24.5122	0.9	0.13251	0.571429	57.14285	-0.87775
	800ppm	23.954	23.104	0.85	0.125149	0.595238	59.52381	-0.90257
	1000ppm	25.3651	24.5651	0.8	0.117787	0.619048	61.90476	-0.9289
313	Blank	27.3231	27.3208	2.3	0.338638	0	0	-0.47026
	400ppm	25.6078	25.6063	1.5	0.220851	0.347826	34.78261	-0.6559
	600ppm	25.6866	25.6853	1.3	0.191404	0.434783	43.47826	-0.71805
	800ppm	25.0456	25.0446	1	0.147234	0.565217	56.52174	-0.83199
	1000ppm	26.4699	26.469	0.9	0.13251	0.608696	60.86957	-0.87775
323	Blank	25.5227	25.5186	4.1	0.603659	0	0	-0.21921
	400ppm	26.7367	26.7338	2.9	0.426978	0.292683	29.26829	-0.36959
	600ppm	26.1711	26.1684	2.7	0.397531	0.341463	34.14634	-0.40063
	800ppm	25.7802	25.7778	2.4	0.353361	0.414634	41.46341	-0.45178
	1000ppm	25.9744	25.9722	2.2	0.323914	0.463415	46.34146	-0.48957
333	Blank	24.7971	24.7919	5.2	0.765616	0	0	-0.11599
	400ppm	25.1948	25.1908	4	0.588935	0.230769	23.07692	-0.22993
	600ppm	24.653	24.6491	3.9	0.574212	0.25	25	-0.24093
	800ppm	22.9033	22.8996	3.7	0.544765	0.288462	28.84615	-0.26379
	1000ppm	21.9187	21.9152	3.5	0.515318	0.326923	32.69231	-0.28792

Key

IW = Initial weight

FW = Final weight

WL = Weight loss

CR = Corrosion rate

Θ = surface coverage

IE = Inhibitor Efficiency

APPENDIX III

Result of Adsorption and thermodynamic analysis

Table 29 Values of activation parameters of Root on the surface of steel in Crude oil

Concentration	E_a (kJ/mol)	ΔH_{ads} (KJ/mol)	ΔS_a (Jmol ⁻¹)
Blank	35.49	35.47	1160.185
400ppm	67.55	67.52	1253.324
600ppm	69.94	69.91	1259.2
800ppm	71.54	71.52	1262.526
1000ppm	73.29	73.89	1268.058

Table 30 Values of activation parameters of Pods on the surface of steel in Crude oil

Concentration	E_a (kJ/mol)	ΔH_{ads} (KJ/mol)	ΔS_a (Jmol ⁻¹)
Blank	35.49	35.47	1160.185
400ppm	42.14	39.46	1166.867
600ppm	47.72	45.04	1181.997
800ppm	51.56	48.87	1192.811
1000ppm	60.1464	57.46	1217.626

Table 31 Values of activation parameters of Leaves on the surface of steel in Crude oil

Concentration	E_a (kJ/mol)	ΔH_{ads} (KJ/mol)	ΔS_a (Jmol-1)
Blank	35.49	35.47	1160.185
400ppm	46.65	43.96	1182.721
600ppm	50.33	47.64	1193.106
800ppm	50.58	47.89	1193.131
1000ppm	50.84	48.15	1192.967

Table 32 Values of activation parameters of Seed on the surface of steel in Crude

Concentration	E_a (kJ/mol)	ΔH_{ads} (KJ/mol)	ΔS_a (Jmol-1)
Blank	35.49	35.47	1160.185
400ppm	42.64	39.96	1171.066
600ppm	47.76	45.07	1186.244
800ppm	56.88	54.19	1213.301
1000ppm	59.03	56.35	1219.277

Table 33 Values of activation parameters of Bark on the surface of steel in Crude oil

Concentration	E_a (kJ/mol)	ΔH_{ads} (KJ/mol)	ΔS_a (Jmol-1)
Blank	35.49	35.47	1160.185
400ppm	37.82	35.14	1193.353
600ppm	44.64	41.96	1180.718
800ppm	47.29	44.61	1166.689
1000ppm	53.52	50.83	1187.379

Table 34: Values of thermodynamic parameters(from Langmuir adsorption isotherm) for the adsorption of Root in Crude oil on steel samples at different temperatures

Temperature (K)	Linear regression coefficient(R^2)	K_{ads} (Mol^{-1})	ΔG_{ads} (KJ/Mol)
303	0.8391	646.83	26.42
313	0.996	944.73	-28.287
323	0.9974	1448.44	-30.338
333	0.9587	953.47	-30.120

Table 35: Values of thermodynamic parameters(from Langmuir adsorption isotherm) for the adsorption of Bark in Crude oil on steel samples at different temperature

Temperature (K)	Linear regression coefficient(R^2)	$K_{ads}(Mol^{-1})$	$G_{ads} (KJ/Mol)$
303	0.8858	771.46	26.87
313	0.9415	857	-28.033
323	0.9537	2276.35	-31.552
333	0.9815	10214.5	-36.687

Table 36: Values of thermodynamic parameters(from Langmuir adsorption isotherm) for the adsorption of Pods in Crude oil on steel samples at different temperature

Temperature (K)	Linear regression coefficient(R^2)	$K_{ads}(Mol^{-1})$	$G_{ads} (KJ/Mol)$
303	0.8921	757.57	26.82
313	0.9904	1134.17	-28.762
323	0.9985	1094.45	-29.585
333	0.9904	805.74	-29.653

Table 37: Values of thermodynamic parameters(from Langmuir adsorption isotherm) for the adsorption of Leaves in Crude oil on low carbon steel samples at different temperature

Temperature (k)	Linear regression coefficient(R^2)	$K_{ads}(Mol^{-1})$	$G_{ads} (KJ/Mol)$
303	0.8705	990.09	27.50
313	0.991	821	-27.923
323	0.9794	848	-28.903
333	0.9794	778	-29.557

Table 38: Values of thermodynamic parameters(from Langmuir adsorption isotherm) for the adsorption of Seed in Crude oil on low carbon steel samples at different temperature

Temperature (k)	Linear regression coefficient(R^2)	$K_{ads}(Mol^{-1})$	$G_{ads} (kJ/Mol)$
303	0.8851	502.97	25.79
313	0.9387	1321.00	-29.159
323	0.9691	785.00	-28.695
333	0.961	459.79	-28.10

APPENDIX IV

RESULT OF MECHANICAL PROPERTIES

Table 39: Impact test result of Samples from the 1000ppm concentration after 33days

SAMPLE	ENERGY Joules(J)
Blank	11.11
Leaves	11.46
Bark	11.39
Root	11.52
Pods	11.25
Seed	11.25

Table 40 Tensile test result of Samples from the 1000ppm concentration after 33days

SAMPLE	MAXIMUM LOAD (kN)	TENSILE STRENGTH (MN/m ²)
Blank	18.0	692
Pods	20.0	741
Bark	19.8	733
Root	19.9	710
Leaves	19.3	715
Seed	19.1	735

Table 41: Rockwell Hardness Number for the Samples of 1000ppm concentration after 33days

Sample	Hardness Value(HRB)
Root	93.9
Leaves	94.2
Bark	94.9
Seed	98.2
Pods	96.1
Blank	92.6