CORROSION INHIBITION OF MILD STEEL USING *LANDOLPHIA HEUDELOTII* AND *OCIMUM GRATISSIMUM* IN ACIDIC MEDIA

BY

OHAEGBULAM CHINYERE ELIZABETH (B.Sc, IMSU)

20124763848

A THESIS SUBMITTED TO POST GRADUATE SCHOOL

FEDERAL UNIVERSITY OF TECHNOLOGY OWERRI,

IMO STATE

DECEMBER, 2016.

CORROSION INHIBITION OF MILD STEEL USING *LANDOLPHIA HEUDELOTII* AND *OCIMUM GRATISSIM* ACIDIC MEDIA

BY

OHAEGBULAM CHINYERE ELIZABETH (B.Sc, IMSU)

20124763848

A THESIS SUBMITTED TO POST GRADUATE SCHOOL
FEDERAL UNIVERSITY OF TECHNOLOGY OWERRI,
IMO STATE

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE AWARD OF THE DEGREE OF MASTER OF SCIENCE
(M.Sc.) IN PHYSICAL CHEMISTRY

DECEMBER, 2016.

CERTIFICATION

This is to certify that this research work **"CORROSION INHIBITION OF MILD STEEL USING *LANDOLPHIA HEUDELOTII* AND *OCIMUM GRATISSIMUM* IN ACIDIC MEDIA"** was carried out by **OHAEGBULAM CHINYERE ELIZABETH** with registration number **20124763848** in partial fulfillment of the requirements for the award of the degree of Master of Science (M.Sc.) in physical chemistry, in the department of chemistry, Federal University of Technology Owerri, Imo state.

06/12/16

Professor E.E.Oguzie
(Supervisor)

Date

Enenebeaku

06|12|16

Dr C.K. Enenebeaku)
(Co - Supervisor)

Date

05-12-2016

Professor M.O.C. Ogwuegbu
(Head of Department)

Date

Professor B.C. Anusionwu
Dean, School of physical Science

Date

Professor Mrs N.N. Oti
Dean, Post Graduate School FUTO

Date

Ubochi

5/12/16

Professor C.I. Ubochi
External Examiner

Date

DEDICATION

This work is dedicated to God Almighty for His guidance, strength and provision, He is the pacesetter, l only follow His lead and through this, this work was accomplished. To Him alone be all glory, honour, and adoration Amen.

ACKNOWLEDGEMENTS

My profound gratitude goes to God Almighty for His grace and strength upon me which saw me through this work. He is the rock on which l leaned on and by His grace this work was accomplished.

I appreciate enormously all the efforts of my amiable supervisor Professor Emeka .E Oguzie, all his assistance, guidance, constructive criticism and scholarly advice contributed immensely to the success of this work. May God Almighty continue to abound you with more wisdom and knowledge to excel in your career, may He also bless and protect your family. In addition, i acknowledge the pertinent efforts of my co – supervisor Dr C. K. Enenebeaku towards the success of this work, I appreciate all your scholarly advice and contribution in this work.

In a most remarkable way, i wish to acknowledge the contributions of my distinguished lecturers and mentors, the head of department of Chemistry, Professor M.O.C. Ogwuegbu, Professor J.I. Alinnor, Prof. C.I. Anunuso, Professor G.N. Onuoha, Professor A.A. Ayuk, Professor U.U. Egereonu, Prof. P.C. Njoku, Dr (Mrs) C. E. Ogukwe, Dr A. E. Ejele, Dr C. I. A. Nwoko. Thank you all for all the vital roles you played towards the success of this programme. May God continue to bestow you with more knowledge, strength, and wisdom to produce scholars in this field.

My appreciation goes to my beloved parents Mr. and Mrs. E.O Ohaegbulam for all their moral support and encouragement all throughout this work which kept me moving despite all odds. I am very grateful, to my siblings Chidinma, Chukwudi, Ugochukwu and Ego. Thank you all for the encouragement. My warm appreciation goes to my darling husband for all his support and encouragement towards this work, I am very grateful and may God continue to bless our union. I am most grateful to my uncle Engr. Emmanuel Nnyagu for his support. May God bless you and your family abundantly I wish to appreciate also all the assistance of Dr Arinze, Dr Nnabuenyi, and Mr Anyanwu. Thank you all for your contributions. I appreciate also all my course mates and friends Nnaemeka, Stella, Nneka, Ada, Ikechukwu, Priestly, Chidinma, Obinna, Ndubuisi, Stanley, Ugochukwu, etc It was wonderful having you guys as course mates and friends. Thank you all for all your contributions one way or the other towards the success of this work.

TABLE OF CONTENTS

CHAPTER ONE

CHAPTER TWO

LITERATURE REVIEW

CHAPTER THREE

CHAPTER FOUR

CHAPTER FIVE

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDIX

APPENDIX I

APPENDIX II

APPENDIX III

APPENDIX IV

APPENDIX V

APPENDIX VI

APPENDIX VII

ABSTRACT

The corrosion inhibition performance of water extracts of *Landolphia heudelotii a*nd *Ocimum gratissimum* on mild steel in 1 M HCl and 0.5 M H_2SO_4 was investigated using weight loss and potentiodynamic polarization technique on mild steel. Results from weight loss analysis revealed that inhibition efficiency increased with increase in concentration of the inhibitors while corrosion rate decreased with increase in concentration of the inhibitors due to the adsorption of the organic molecules on the metal surface. Highest inhibition efficiency of 97.27% and 94.31% was recorded in *Ocimum gratissimum and Landolphia heudelotii* at 2500mg/l in 1M HCl after twelve days respectively. Temperature studies also revealed the inhibition efficiencies of both extract at the temperature ranges of 313 K - 333 K, highest inhibition efficiency of 97.60% and 95.84% was recorded in *Ocimum gratissimum and Landolphia heudelotii i*n 1 M HCl respectively at 323 K and 2500 Mg/l. From the values of activation energy obtained, the mechanism of the adsorption process was proposed to be predominantly of physisorption in both plant extracts. The values of ΔG obtained reveals spontaneity of the process while ΔH_{ads} reveals endothermic and exothermic reactions occurring in 0.5 M H_2SO_4 and 1 M HCl in both plant extracts respectively. Potentiodynamic polarization results showed that both the anodic and cathodic reactions were inhibited indicating that the inhibitors are of mixed type. The experimental data obtained fits well with Langmuir adsorption isotherm indicating that the inhibitors were adsorbed uniformly on the metal surface. The mechanism of adsorption was proposed to be as a result of the bonding of the free electrons of the inhibitor with the metal surface due to electrostatic force of attraction existing between inhibiting organic ions and the electrically charged metal surface at the metal/solution interphase.

Keywords: Corrosion inhibition, mild steel, corrosion rate, inhibition efficiency, adsorption, *Landolphia heudelotii, Ocimum gratissimum..*

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND INFORMATION

Mild steel is used extensively in various industries like food, sugar, leather, petrochemical and textile industries. Corrosion of metals is a common problem that has economical as well as environmental impact. Many of the corrosion problems encountered in our industries today involves acids such as HCl and H_2SO_4 used frequently in cleaning, prickling, descaling, acidizing in mining and oil wells (Abdallah *et al.*, 2001; Ishtiaque *et al.*, 2010). Hence corrosion inhibition in acid media becomes a necessity. Corrosion has a lot of economic impact especially in our industries where metals are used in constructing equipments and structures, it has also caused important material and economic losses due to partial or total replacement of equipments / structures and plant repair shutdowns. Globally corrosion is an accepted industrial challenge, in the U.S economy the estimated cost of metal corrosion is almost $300 billion per year and approximately one third of these can be avoided by the use of corrosion resistance materials and application of best corrosion related technical practices, hence, there is need to reduce or control corrosion. Corrosion inhibitors have been developed by chemist and corrosion engineers through researches in other to reduce rate of corrosion of metals and alloys. Over the years the use of synthetic organic and inorganic corrosion inhibitors have proven to be hazardous to health as well as the environment. Synthetic inhibitors are highly toxic, expensive, not readily available, non – biodegradable, non-renewable and more especially, are not eco- friendly, as a result, a lot of researches have been focused on the provision of alternative source of corrosion inhibitor that is environmentally accepted (Kumasi *et al.,* 2009; Nnanna *et al.,*2011; Oguzie *et al.,* 2007; Otti *et al.,*1995; Shymal *et al.,* 2011). The discovery of corrosion inhibitors from plant origin has provided an alternative source of corrosion inhibition, plant materials such as the leaves, barks and fruits contains phytoconsistuents such as tannins, saponins, flavonoids which have been proven to be the major constituents present causing inhibition. These phytoconsistuents contains lone pair of electrons present on a hetero- atom (i.e oxygen, phosphorous, sulphur and nitrogen), pi- bond, triple bond (e.g cyano group) in their functional group which are characteristics of a good corrosion inhibitor (Bendahou, 2006; Minhaji, 1999; Odiongenyi, 2006). The inhibitors used in this study are from plant origin therefore are environmentally accepted, biodegradable, cheap, renewable, readily available and less toxic

1.2. Definition of Corrossion

The term corrosion has its origin in Latin, 'rodere' signifying gnawing to pieces. Corrosion is defined as the deterioration of materials by chemical interaction with the environment causing slow, steady and irreversible deterioration of the metal in both physical and chemical properties (Sastri *et al.,* 2007). It is also defined as an electrochemical process by which metallic surfaces reacts with their environment causing the metal to lose its material properties due to surface deterioration (Boyanzier *et al.,* 2005; El-Rehim *et al.,* 2001). Virtually all metals with exception of gold and platinum corrodes in an oxidizing environment forming compounds either in their oxides, hydroxides and sulphates (Ashworth, 1996; Nasa-Nasa, 1994; Vasant & Bansal, 2013). Corrosion causes important material and economical loses due to partial or total replacement of equipment and structures and plant repairing shutdowns (Fontana *et al.,* 1967; Sastri *et al.,* 1998).

1.3. The Economic Impact of Corrosion

In the U.S economy corrosion of metals has cost almost $300 billon per year at current prices. Approximately one-third of this cost can be avoided by the application of corrosion resistant materials and the application of best corrosion –related technical practices .This estimate is the result from a recent update of 1978, study of economic effect of metallic corrosion in the United State performed by Battelle Columbus laboratories and the National Institute of standards and Technology (NIST) published in April 1995. In 1975 metallic corrosion cost United State $82 billon or 4.9% of its gross National product (GNP) of which 60% is avoidable while 33% was incurred by failure to use the best practices known (Anderson, 1995; Coburn, 1984; Craig & Graver,1985).

1.4. Causes of Corrosion

The factors that can cause corrosion can be identified as follows: physical factors, chemical factors, electrochemical factors and microbiological factors.

1.4.1. Physical and chemical factors

Physical factors is caused by impact stress or exhaustion of the material while chemical factors is caused by the presence of oxygen, sulphur, fluorine, chlorine or other gases which act directly on the metal under environmental condition that facilitate the phenomenon.

1.4.2. Electrochemical and microbiological factors

Electrochemical factors involves a spontaneous process that denotes the existence of anodic and cathodic zones and an electrolyte which serves as an electrical contact between the anodic and cathodic zones. In microbiological factor, deterioration of a metal occurs directly or indirectly as a result of the activity of microorganism such as bacteria and algae. The microorganism are deposited on the metal creating a ”live” area using nitrogen, oxygen, hydrogen and carbon from the environment for metabolic activities producing metabolites which can be deposited on the metal promoting corrosion (Revie & Uhlig, 2008).

1.5. Corrosion as an electrochemical process

Corrosion is an electrochemical process involving anodic and cathodic reaction .The rate of anodic and cathodic reaction is equivalent to faraday’s law (Ashworth *et al* 1998). The chemistry of the reaction involved are as follows

1.5.1 Anodic reaction (oxidation site)

$$Fe + 2e \rightarrow Fe^{2+} \qquad (1)$$

1.5.2 Cathodic reaction (reduction site)

Two possible reaction can occur

$$2H + 2e \rightarrow H_{2(g)} \qquad (2)$$

$$H_2 + \frac{1}{2}O_2 + 2e \rightarrow 2OH^- \qquad (3)$$

This is accompanied by the formation of solid debris from reaction of anodic and cathodic products.

$$Fe + 2OH^- \rightarrow \underset{\text{(Iron ll hydroxide)}}{Fe(OH)_2} \qquad (4)$$

On further oxidation hydrated iron III oxide is formed.

$$Fe(OH)_2 + H_2O + \frac{1}{2}O_2 \rightarrow \underset{\text{(Hydrated iron Ill oxide)}}{2Fe(OH)_3} \qquad (5)$$

3.2 Types of corrosion

Physiochemically, corrosion is divided into the following seven categories as follows:- uniform corrosion, pitting corrosion, corrosion by erosion, stress corrosion cracking, galvanic or bimetallic corrosion, corrosion via hydrogen embrittlement and blistering and corrosion by cavitation

1.6.1 Uniform corrosion:

This is the most common type characterized by the corrosion occurring uniformly over the metal surface and it has a high corrosion rate. The loss of the metal surface occurs at the anodic sites while the appearance of the corroded surface is relatively uniform and manifests roughness (Levy, 2002).

1.6.2 Piting corrosion

This is a form of localized attack where some part of the metal surface are free of corrosion but small localized area corrode quickly. This occurs when any solid corrosion product or neutralization salt are located on the metal surface causing deep holes known as “piting”, these areas are the most susceptible to the corrosion process (Marcus *et al* 2008).

1.6.3 Corrosion by erosion.

This type of corrosion provokes uniform thinning of the metal surface which is associated with the exposure to high velocity fluid which causes the erosion product to be stripped from the metal surface resulting in the exposure of the bare metal surface which can corrode again causing an accelerated attack (Levy, 2002).

1.6.4 Stress corrosion cracking.

This type of corrosion promotes the formation of a fracture in the metal structures due to mechanical stress and a chemically aggressive medium (Sieradzki & Newman, 1987).

1.6.5 Galvanic or Bimetallic corrosion.

This occurs when there is a potential difference between dissimilar metal immersed in a corrosive solution, the potential difference produces flow of electrons between the metals where the less resistance is the anode (metal active) and the most resistance is the cathode (noble metal). The attack can be destructive dramatically accelerating the corrosion rate of the most reactive metal (Song *et al.*, 2004).

1.6.6 Corrosion via hydrogen embrittlement and blistering:

This is associated with the hydrogen atoms that can be produced on the metal surface in an aqueous medium, a reduction reaction occurs when atomic hydrogen penetrates the metal. The presence of defects allow the interaction between the hydrogen atoms and the metal forming molecular hydrogen which can be trapped by the metal producing enough pressure to form blisters resulting to micro-cracks. This occurs mainly in basic media where there are compounds such as sulphides or cyanide (Gonzalez *et al.*, 1997).

1.6.7 Corrosion by cavitation:

This is a form of corrosion caused by the formation and rupture of vapour bubbles in the fluid near the metal surface causing sequence of pits in the form of small but deep cracks (Al-Hashem & Riad-Wet, 2002).

1.7 Corrosion Measurement and Monitoring.

1.7.1 Corrosion measurement

This is the quantitative method by which the effectiveness of corrosion control and prevention technique can be evaluated. lt provides feedback to enable corrosion control and prevention methods to be optimized. A variety of technique can be employed and they are:

1.7.2 Non destructive testing Analytical Chemistry:

This includes use of ultrasound testing, radiography, thermography, eddy current / magnetic flux and intelligent pigs in measuring the effectiveness of a corrosion control and prevention technique (Devalapura *et al* 1994). It also involves pH measurement, dissolved gas (O_2, CO_2 ,H_2S), metal count (Fe^{2+}.Fe^{3+}), microbiological analysis in measuring the effectiveness of a corrosion control and prevention technique.

1.7.3 Operational Data :

This includes pH, flow rate (velocity), pressure, temperature in measuring the effectiveness of a corrosion control and prevention technique.

1.7.4 Fluid Electrochemistry In fluid electrochemistry, potential measurement, potentiostatic and potentiodynamic measurements and A.C impendance are used in measuring the effectiveness of a corrosion control and prevention technique.

1.8. Corrosion monitoring:

This is the practice of measuring the corrosivity of a process stream conditions using probes which are inserted into the process stream and are continuously exposed to the process stream conditions (Miksic *et al.*, 1999). The common corrosion monitoring techniques are as follows:

- Corrosion coupons (Weight Loss measurements)
- Electrical resistance (ER)
- Linear polarization resistance
- Galvanic (ZRA) potential
- Hydrogen penetration
- Microbial (Pierre *et a*l., 2007).

1.8.1 Corrosion coupons (weight loss measurements).

This is the best known and simplest of all corrosion monitoring techniques. In this technique the specimen of material (coupon) is exposed to a process environment for a given duration then removed for analysis. The basic measurement determined from corrosion coupons is weight loss which is the weight loss taking place over the period of exposure expressed as corrosion rate.

1.8.2 Electrical resistance (ER) monitoring.

Electrical resistance probes are electronic corrosion coupons which provides a basic measurement of metal loss but unlike coupons the value of metal loss can be measured anytime while the probe in-situ are permanently exposed to the process stream. The ER techniques measures the change in ohmic resistance of a corroding metal element exposed to the process stream. The action of corrosion on the surface of the element produces a decrease in its cross-sectional area with corresponding increase in its electrical resistance. This increase can be related directly to metal loss and the metal loss as a function of time by definition is the corrosion rate (Lemoine *et a*l., 1990).

1.8.3 Linear polarization resistance (LPR) monitoring.

The LPR technique is based on complex electro-chemical theory. LPR is applicable in industrial measurement. In this technique a small voltage (or polarizable potential) is applied to an electrode solution. The current needed to maintain a specific voltage shift (ie 10mv) is directly related to the corrosion on the surface of the electrode .Thus by measuring the current, a rate can be derived. The advantage of the LPR is that the measurement of corrosion rate is made instantaneously unlike in coupons and ER. The disadvantages of the techniques is that it can only be successfully performed in a relatively clean electrolytic environment thus it does not work in gases or water /oil emulsion where fouling of the electrodes prevents measurement to be made (Papavinasam, 2008).

1.8.4 Galvanic/potential monitoring

This is also known as Zero Resistance Ammetry (ZRA). ln this techniques ZRA probes, two electrodes of dissimilar metals are exposed to the process fluid. A natural voltage, potential difference exist between the electrodes when immersed in solution. The current generated due to this potential difference is related to the corrosion occurring on the active electrodes couple. Galvanic potential monitoring is applicable to the following couples.

- Bimetallic corrosion
- Crevice and pitting attack
- Corrosion by assisted cracking
- Corrosion by highly oxidizing species (Elsener *et al.*, 1994).

1.8.5 Specialised monitoring:

This includes the following –

1.8.5.1 Biological monitoriing. Biological monitoring and analysis identifies the presence of sulphate reducing bacteria (SRB'S). This is a class of anaerobic bacteria which consumes sulphate from the process stream and generates sulphuric acid a corrossive which attacks production plant materials.

1.8.5.2 Hydrogen penetration monitoring.

This involves the use of hydrogen probes to detect the amount of hydrogen permeating through steel by mechanical or electrochemical measurement and to use this as a quantitative indication of corrosion rate.

1.9. Electrochemical principles and potentiodynamic polarization measurement

Potentiodynamic refers to polarization in which the potential of the electrode is varied over a relatively large potential domain at selected rate by application of a current through the electrolyte. Potentiodynamic polarization is used for laboratory corrosion testing (Kumaravel *et al* 2011; Morris & Scarberry, 1972; West, 1970). It provides significant useful information regarding corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion designated materials. Investigations such as passivation techniques and effects of inhibitors and oxidizers on specimen are easily performed with the technique (Stern & Geary, 1957).

A metal specimen immersed in a corrosive medium undergoes reduction and oxidation reactions at its surface Typically the specimen oxidizes (corrodes) and the medium (solvent) is reduced . A specimen in contact with a corrosive liquid without contact to any instrumentation assumes a potential relative to the reference electrode termed the corrosion potential (E_{corr}). A specimen at E_{corr} has both anodic and cathodic current present on its surface. Electrode potential (E_{corr}) is the potential at which the rate of oxidation is exactly equal to the rate of reduction. If the specimen is polarized more positive than E_{corr} then the anodic curve predominates at the expense of the cathodic current, on the otherhand , if the specimen is polarized in the negative direction, the cathodic current predominates and the anodic components becomes negligible (Stern & Greary, 1957).

1.9.1. Polarization resistance

A polarization resistance measurement is performed by scanning through a potential range that is close to the corrosion potential (E_{corr}). The potential range is generally ±250mV about E_{corr} .The resulting current is plotted versus potential. The corrosion current is related to the corrosion rate by the equation below:

$$\text{Corrosion Rate(mpy)} = \frac{0.13 I_{corr}\ (E.W)}{d} \tag{6}$$

where E.W = equivalent weight of corroding species

d = density of the corroding species in g/cm^2

I_{corr} = corrosion current density (Morris & Scarberry, 2000).

1.9.2. Tafel plot

A Tafel plot is performed on a metal specimen by polarizing the specimen about 300mV anodically (positive going potential) and cathodically (negative going potential) from the E_{corr}.

The corrosion current is obtained from Tafel plot by extrapolating the linear portion of the curve to E_{corr} :

1.10. Corrosion control

Corrosion control can be done using any of the following method namely cathodic protection, protection with anti corrosive coatings and corrosion inhibitors**.**

1.10.1 Cathodic protection and protection with anticorrosive coatings

Cathodic protection is an effective way of controlling corrosion on structures either buried or immersed in an electrolyte. According to the operation mode, anode are classified as impressured current and sacrificial (Agarwal & Landolt, 1999). In proctection using anti corrosive coatings it involves use of physical barrier between the corrosive environment to protect the structure. It is used mainly with metallic elements exposed to the atmosphere.

1.10.2 Corrosion inhibitors

Corrosion inhibitors are either organic and inorganic formulations that are added in small quantities (parts per millions) to a corrosive environment in order to delay or decrease the corrosion process of the surface to be protected (Hubert *et al.,* 2002; Revie, 2008). They are formulations generally made up of one or more active ingredients and suitable vehicles (other addictives and solvents) that encourage compatibility with the environment and make viable the active transport to the area to be protected (metal surface) (Singh *et al.,* 2012).

1.11. Classification of corrosion inhibitors.

Corrosion inhibitors can be broadly classified into two based on their mode of interaction with metal surface as follows:

- Environmental modifiers inhibitors
- Adsorption inhibitors.

1.11.1 Environmental modifiers inhibitors

These are corrosion inhibitors whose action and mechanism involves simple interaction with the aggressive species in the environment thereby reducing the attack of the metal, examples oxygen scavengers such as hydrazine or sodium sulfite along with colbaltous nitrate and biocidies used in inhibiting microbiological corrosion..

1.11.2 Adsorption inhibitors.

Many inhibitors work by adsorption mechanism. The film of chemisorbed inhibitor is responsible for the protection either by physically blocking the surface from the corrosive environment or by retarding the electrochemical process. The functional group that forms the chemisorbed bonds with metal surface are amino (NH_2), carboxyl (-COOH) and phosphate (-PO_3H_2). Adsorption inhibitors are classified into the following

1.11.3 Anodic inhibitors

These are inhibitors that interfere with anodic process .They inhibit the oxidation of the metal.

$$Fe + 2e \rightarrow Fe^{2+} \qquad (7)$$

They are generally effective in the pH range of 6.5 -10.5 (near neutral or basic), examples are oxyanions , orthophosphate, nitrite, ferric cyanide and silicates.

1.11.4 Cathodic inhibitors

These are inhibitors that inhibit hydrogen evolution in acidic solution or the reduction of oxygen in neutral or alkaline solution (Hackerman & Snavely, 1984).

$$\frac{1}{2}O_2 + H_2O + 2e \quad \rightarrow \quad 2OH^- \tag{8}$$

1,11.5. Mixed inhibitors

These inhibitors are generally represented by organic compounds. This involves the incorporation of both anodic and cathodic inhibitors in corrosion control and prevention, it functions as both anodic and cathodic inhibitor. The inhibition process involves the transport of inhibitor to the metal sites followed by the interaction of the inhibitor with the surface of the metal resulting in protection (Chen *et al* 2013; Hauser, 1983).

1.11.6. Volatile corrosion inhibitor.

Volatile corrosion inhibitors also called vapour phase inhibitor (VPI) are compounds transported in a closed environment to the site of corrosion by volatization from a source, examples of such inhibitors are morpholine or hexamethyleneamine (Landolt, 1998).

The use of synthetic and inorganic inhibitors are toxic and detrimental to health, as a result corrosion inhibitor from plant extracts are employed (Singh et al 2012). These inhibitors are eco-friendly, inexpensive, rich in natural biodegradable chemicals and abundantly available (Abiola , 2007 ; Ambush et al 2010; Omotosho, 2012). The organic compounds contain tannin, alkaloids, saponins which are responsible for the inhibiting trait found in green inhibitors (Garber *et al.*, 2008; Raja *et al.*,2013).

1.12 Inhibition mechanism.

The mechanism of corrosion inhibition are outlined as follows:

- Adsorption, forming a film that is adsorbed onto the metal surface.
- Inducing the formation of a corrosion product such as iron sulphide which is a passavating specie.
- Changing the media characteristics by producing precipitates that can be protective and eliminating or inactivating an aggressive constituent (Umoren & Ekanem, 2010).

1.13 Corrosion protection and control:

Corrosion protection and control are classified into the following active corrosion protection, passive corrosion protection, permanent corrosion protection and temporary corrosion protection.

1.13.1 Active and passive corrosion protection

Active corrosion protection involves the development of corrosion resistant alloys and addition of inhibitors to the aggressive medium to influence the reaction which proceed during corrosion. In passive corrosion protection protective layers, films or other coatings are used to mechanically isolate the package contents from aggressive corrosive agents.

1.13.2 Permanent and temporary corrosion protection

Permanent corrosion protection provides protection at the place of use from stresses presented by climatic, biotic and chemical factors. Examples of such methods are tin plating, galvanizing, enameling and coating. In temporary corrosion protection it is applied for stresses occurring during transport, handling and storage occurring at the place of use e.g in maritme transport where the salt content is high causes damage because of its strong corrosion –promoting action

1.14 Methods of corrosion control.

There are basically five (5) methods of corrosion control namely: material selection, coatings, cathodic protection, design and inhibitors.

1.14.1 Material selection

Material selection is one of the ways of controlling corrosion. Each metal and alloy has unique and inherent corrosion behaviour that ranges from high resistance noble metal such as gold and platinum to low resistance active metals such as sodium and magnesium**.**

1.14.2 Coatings:

Coatings applied for corrosion protection are divided into two broad groups namely metallic and non –metallic (organic and inorganic) (Drisko & Jenkins, 1998).

1.14.2.1 Metallic coatings

This involves coatings of a more noble metal coating on an active metal example is tin –plated steel. Alternatively a more active metal can be applied and in this case the coating corrodes prefentially or sacrificially to the substrate, example is galvanized steel where the sacrificial zinc corrodes preferentially and protects the steel.

1.14.2.2 Organic and inorganic coatings

The primary function of organic coatings in corrosion protection is to isolate the metal from the corrosive environment by forming a barrier to stifle corrosion, the organic coating contain corrosion inhibitors, Jones, (1996). Inorganic coatings serves as barrier coatings examples porcelain enamels, chemical- setting silicate cement linings, glass coatings and lining and other corrosion resistant ceramics.

1.14.3 Inhibitors:

These are some chemical species that inhibit corrosion examples are chromates, silicates and organic amines are common inhibitors. Inhibitors function by altering the anodic or cathodic sites of the corrosion process while others promotes the formation of protective films on the metal surface. Inhibitors are incorporated in a protective coating, at a defect in the coating the inhibitor leaches from the coating and controls the corrosion (Dekker, 1989)

1.14.4 Cathodic protection

Cathodic protection suppresses the corrosion current that causes damages in a corrosion cell and forces current to flow to the metal structure to be protected, thus the corrosion or metal issolution is prevented.

1.14.5 Design:

This involves the application of rotational design principles to eliminate corrosion. Corrosion often occurs in dead spaces or crevices where the corrosive medium becomes more corrosive. These areas can be eliminated or minimized in the design process (During, 1997).

1.15. PROBLEM STATEMENT

The corrosion of metal at the solid –liquid interphase is a major problem encountered in our society today,.

- Corrosion of metals in a corroding environment is practically unavoidable because metals are thermodynamically unstable in the environment.
- Since corrosion of metals is inevitable, there is need to know how long equipment and structures will serve safely and efficiently under particular conditions.
- Corrosion of metals varies depending on the type of metal and environment.
- Thus it is scientifically necessary to select best material for a given environment and with the knowledge of corrosion rate , corrosion type, the durability of an equipment can be predicted.

1.16. AIM OF STUDY:

This work is focused on the use of organic inhibitor of plant origin which contains phytochemicals in solving the problem of corrosion, consequently developing new, more efficient and environmentally friendly additives which are cheap and renewable

1.17 SPECIFIC OBJECTIVES

- To determine the inhibition performance of *Landolphia heudelotii* and *Ocimum gratissimum*
- To investigate the effect of temperature on the corrosion rate and inhibition efficiencies of selected plants of interest.
- To determine some thermodynamic parameters from temperature studies
- To determine the possible mechanism of the inhibition process from temperature studies.

1.18. JUSTIFICATION

Plants extracts are organic inhibitors containing phytochemicals such as tannin, alkaloids, saponins and terpenoids with molecular & electronic structures similar to those of conventional corrosion inhibitors.

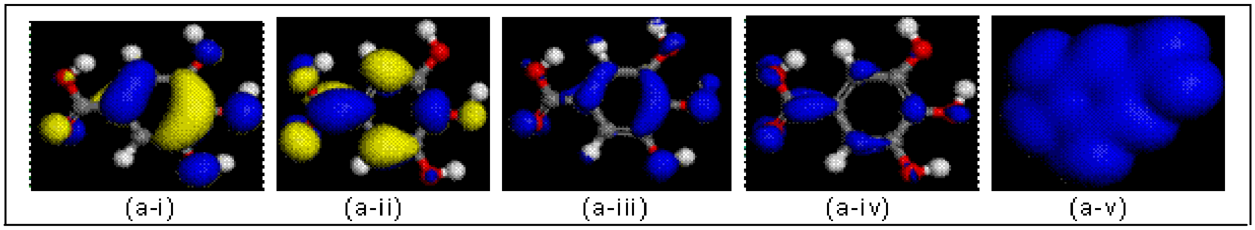

Fig. 1.1: Typical Organic Inhibitor Molecules

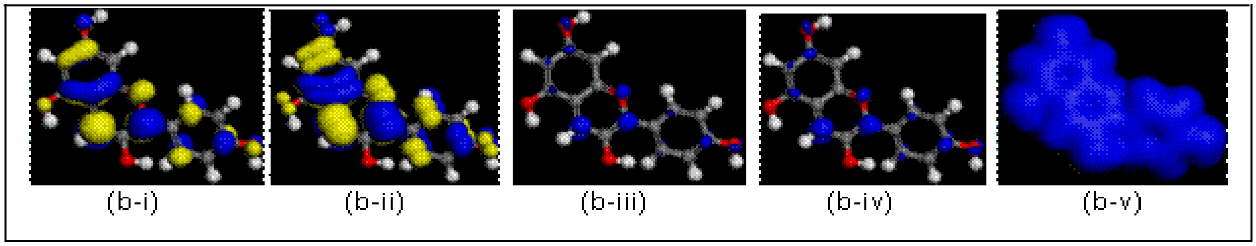

Fig. 1.2: Typical Phytochemical Constituent Inhibitor Molecules

1.19 SIGNIFICANCE OF THE STUDY

- Plants are recognized as sources of naturally occurring compounds, their extracts have been applied over the years as excellent corrosion inhibitors
  .
- The use of naturally occurring compounds of plant origin are of interest because they are cost effective, abundant, readily available, non toxic and more importantly eco -friendly.
- Organic inhibitors from natural products like other conventional inhibitors act by adsorbing on the metal surface to form an insoluble organic complex compound with the corroding specie hence reducing and preventing its attack on the metal surface.
- The use of weight loss technique (gravimetric) and potetiodynamic polarization are applied in the study of inhibition efficiencies of the selected plant extracts.

1.20 SCOPE OF THE STUDY

The scope of the study covers the assessment of organic inhibitor from plant origin in the corrosion inhibition of mild steel in 1 M HCl and 0.5 M H_2SO_4 respectively. Weight loss and potentiodynamic polarization techniques are applied in this study to monitor inhibiting effectiveness of the selected plant extracts as corrosion inhibitors in the two test media. Temperature studies was also carried out to determine some thermodynamic parameters such as activation energy, Gibb’s free energy and change in enthalpy, hence, suggest the possible mechanism of adsorption process while electrochemical method (potentiodynamic polarization technique) was carried out to determine some corrosion kinetic parameters such as corrosion current density, I_{corr}, corrosion electrode potential, E_{corr} and to determine the type of inhibitor from the polarization curves.

CHAPTER TWO

LITERATURE REVIEW

2.1. METALLIC CORROSION INHIBITOR OF PLANT ORIGIN

The use of phytochemicals as corrosion inhibitor can be traced to 1960's when tannin and derivatives were used to protect corrosion of steel, iron and other tools. In the study by El Hosary et al. (1972) on the use of common plant extract of tobacco from stems, twigs as well as leaves as corrosion inhibitors, result from their study showed significant corrosion inhibition of aluminum and steel in both saline solution and strong prickling acid.

Extract from leaves were investigated and found to be effective corrosion inhibitors for mild steel in 2 M HCl solution. The authors reported maximum inhibition efficiency of 96% with only 0.01% tobacco concentration(100ppm). Tobacco extract is reported to contain high concentration of chemical compounds including terpenes, alcohols, polyphenols, carboxylic acids, nitrogen containing compounds and alkaloids that exhibit electrochemical activity such as corrosion inhibition (Davis *et al.,* 2001). Srivastava and Srivastava (1981) investigated the inhibition effect of tobacco, black pepper, castor seed, Acacia gum and lignin and are found to be good corrosion inhibitor for steel in acidic media. Tobacco, lignin and black pepper were also found to be effective inhibitor for aluminum in acid medium. Further research on castor seed, black pepper and lignin on carbon steel corrosion in 5% HCl solution obtained 60 -70% inhibition efficiency (Quarishi *et al.,* 2004). Saleh *et al.* (1982) carried out an intensive study on the inhibition effect of aqueous extract of *Opuntia ficus lndica,* Aloe eru leaves and peels of orange, mango and pomegranate fruit on the corrosion inhibition of steel, aluminum, zinc and copper in both HCl and H_2SO_4 acid solution using gravimetric and polarization measurement technique. From their investigation it was reported that mango peel extract was the most effective corrosion inhibitor for Al and Zn where as pomegranate fruit shells extract was most suitable for Cu. It was further reported that all the extract were more effective corrosion inhibitors in HCl solution as compared to H_2SO_4 solution.

Pravinar et al. (1993) reported the inhibitive effect of aqueous extract of Eucalyptus leaves in the corrosion of mild steel and copper in 1M HCl solution .The inhibition efficiency was investigated by galvanostatic polarization, mass loss measurements and surface characterization technique. The inhibition efficiency was found to increase with increase in concentration of the extract and decrease with increase in temperature. The extract was found to be a mixed type inhibitor (i.e both cathodic and anodic reactions) predominantly of cathodic control.

The inhibitive effect of pomegranate alkaloids on acid corrosion of mild steel in H_2SO_4 were also investigated by Aymen and Singh (1991) using galvostatic polarization and mass loss measurement at different temperature. It was found that pomegranate alkaloids have a good efficiency at low temperatures. The observed efficiency was explained to be due to the metal additive complex formation.

Soltani and khayatkashani (2014), investigated the inhibition effect of *Gundelia tournefortii* on mild steel in 2 M and 1M H_2SO_4 using weight loss, potentiodynamic polarization and electron impendance spectroscopy. Results from their work showed that G. *tournefortii* is a good corrosion inhibitor of mild steel in both test media. Potentiodynamic result revealed that G.*tournefortii* extract follows the mixed type corrosion inhibition in both acid solution. Temperature result revealed a decrease in efficiency with rise in temperature. Comparatively their results from both acid solution suggest a protonated and neutral organic species maybe responsible for the observed inhibitive behaviour and the predominant effect is the physical adsorption of the protonated species.. The adsorption of the extract was found to obey Langmuir adsorption isotherm.

Subhashini (2004) studied the inhibition effect of seed extract of *Alfa alfa* (Aa), *Adenanthera pavonia* (Ap), *Phaseolus* (Pt) and *Sesbania grandiflora* (Sa). The seed extract were tested as corrosion inhibitors of mild steel in 1M HCl and 0.5M H_2SO_4 at various immersion time and concentration. Inhibition performances were assessed using mass loss, polarization and electrochemical impedance spectroscopy and optical microscopy. The surface of mild steel tested were analyzed using Fourier transform infra red spectroscopy and optical microscope. Their result clearly indicated the decrease in corrosion rate with increase in concentration of the extract as well as increase in immersion time. All extract investigated showed maximum eff,kiciency of 0.7% extract concentration. The corrosion inhibition performance of the extract decreased in the following order: Sg > Aa > Pt > Ap >Pl > in HCL and Pt > Aa > Pl > Sg > Aa in $H_2SO_{4.}$ However these extract showed a better inhibition performance in HCl than in H_2SO_4. This was explained to be due to the adsorption of chloride ions on the metal surface than sulphate ions prefentially.

The aqueous extract of the leaves of Henna (Lawosonia) has been tested as corrosion inhibitors of carbon, steel, nickel and zinc in acidic, neutral and alkaline solution using polarization technique (El – Etre *et al.*, 2005). Lawsonia is cultivated in Africa and Asia for medicinal and dyeing purposes. lt was found that the extract acts as a good corrosion inhibitor for the three metals in all tested media. El -Etre *et al.* (2005) postulated that the degree of inhibition depended on the nature of the metal and the type of the medium. For steel and nickel, the inhibition efficiency increased in the order alkaline < neutral < acidic while in case of zinc it increased in order acid < alkaline < neutral thereby reconciling with observed concept of the Lawsonia extract being a mixed inhibitor. The inhibitive action of the extract was discussed in view of the adsorption of the complex Lawsonia molecules into the metal surface. El –Etre *et al.* (2005) found that this adsorption followed Langmuir adsorption isotherm in all tested systems. They also proposed that the formation of the complex between the metal cation and Lawsone (2 – hydroxyl -1, 4-naphthoquinone) was an additional inhibition mechanism of steel and nickel corrosion.

El and El – Tantawy (2006), reported the inhibitive action of Ficus towards general and pitting corrosion of carbon, steel, nickel and zinc in different aqueous media. The study was performed using weight loss measurement, potentiostatic and potentiodynamic polarization techniques. It was found that the presence of Ficus extract in the corrosive media (acidic, neutral or alkaline) decreased the corrosion rate of the three tested metals significantly.

The extract of Henna leaves as environmentally friendly corrosion inhibitor of metals was also investigated by Al –Sebaibani (2000), the water extract of Henna, Lawsonia inermis leaves powder was evaluated as corrosion inhibitor for mild steel in saline, acid and alkaline water. The maximum efficiency attained by just 200g/L of the extract was up to 96% and observed no inhibition for steel and aluminum in NaCl solution .

Chaieb *et al.* (2005) investigated the effect of eugenol and its derivative (acety –leugenol) extracted from nail of giroflier (*Eugenia Caryophyllata*) on the corrosion inhibition of steel in 1M HCl solution. Weight loss measurement, electrochemical polarization and electrochemical impedance spectroscopy methods was used. Eugenol and acetyleugenol belongs to the class of compounds called Vanilloids. These compounds are known to have some antioxidant properties and diets containing these antioxidants can reduce the risk of diseases such as cancer and possibly malaria aids and ageing effects (Chaieb *et al.,* 2005). It was observed that the extracts reduce corrosion rate of steel in 1M HCl significantly. Their inhibition efficiencies were found to increase with eugenol and attained 80 – 91% at concentration of 0.173g/l respectively. This implies that acetyleugenol is more active to the surface as compared to eugenol due to the presence of the carbonyl group. Similarily, the effect of temperature was also investigated at maximum concentration of both eugenol and acetyleugenol at 0.173g/L. The result indicated that as the temperature increases the inhibitor performance changed from 64% at 298 K to 87% at 328 K. The adsorption of these extract on the metal surface was reported to follow Langmuir adsorption isotherm.

Some essential oils also have been investigated as green corrosion inhibitor examples are Ginger, Henna, Jojoba oil and Artemisia oil , they are reported to have very efficient corrosion inhibition for iron and steel in acidic media (Bouyanzer & Hommouti, 2004; Chetouani et *al*., 2004). The effect of naturally occurring extract of Artemsisia on the corrosion of steel in 0.5M H_2SO_4 in the temperature range of 298 K-353 K was studied using weight loss, electrochemical polarization and linear polarization methods (Bouklah & Hammouti, 2006). The result obtained revealed that the extract reduces the corrosion rate quite significantly .The inhibition efficiency increases with the increase of Artemisia content at 10g/L to reach 95% and 99% at 298 K and 353 K respectively. The inhibition efficiency increased with temperature and it was found that the adsorption of Artemisia extract on the steel surface follows Langmuir adsorption isotherm. Similar result were investigated on the Artemisia oils on the corrosion of steel in HCl (Bendahou *et al* .,2006; Bouklah & Hammouti, 2004). Artemisia was found to be a good and potent anti-malaria drug and divanone has been found to be its major consistent (Benjilali *et al.*, 1982). Since divanone is a diketone compound the inhibitory action was interpreted to be the formation of Fe (ll) –Divanone complex.

Rehan (2003), conducted a research on the effect of the water extract from dry leaves of economic plants, date palm *(phoenix dectylifera)*, Henna *(Lawsonia innermis)* and corn *(Zea mays)* on the corrosion inhibition of commercial grade metals, steel, aluminum and copper in acidic chloride and sodium hydroxide solution using weight loss, solution analysis and potential measurements. The inhibition action was found to critically depend on the metal type and solution composition. Only date palm and henna extract were found highly effective in reducing corrosion rate of steel in acidic chloride solutions. The inhibition efficiency increased with increasing concentration of the extract. The inhibition was interpreted in terms of chemisorptions of some active ingredients in the leaves according to Temkin isotherm. The leaves of date palm and corn are generally by-products and used chiefly in Basketry and animal feeding respectively. Henna leaves are used as hair dyestuff and in shampoo industry due to pleasant dermatological effect (Rehan, 2003).

Onuegbu *et al.* (2013) researched on *Emila Sonchifolia* extract as green corrosion inhibitor of mild steel using weight loss at temperature ranges of 30^0C to 60^oC and electrochemical techniques (potentiodynamic polarization) revealed that the extract retarded the corrosion rate of mild steel. The inhibition efficiency increased with increase in concentration of the extract up to 74.77% at 1.0 M. Increase in temperature increased the corrosion rate in the absence and presence of the inhibitor. Temperature studies revealed the phenomenon of physical adsorption from the activation parameters obtained. Thermodynamic parameters obtained indicated that the adsorption process is spontaneous. Potentiodynamic polarization indicated that the inhibitor is of mixed type and experimental data obtained obeyed Langmuir adsorption isotherm indicating that the inhibitor was adsorbed on the surface of the mild steel.

Hui Cang *et al.(* 2013) investigated the corrosion inhibition of mild steel by Aloes extract in 1M HCl solution using weight loss, potentiodynamic polarization and electron impedance spectroscopy. Results of their studies revealed that the inhibition efficiency increased with increase in extract concentration. Temperature studies revealed that the corrosion rate and inhibition efficiency decreased with increase in temperature. Potentiodynamic polarization indicates the inhibitor to be of mixed type. The adsorption of the extract molecules on the mild steel surface obeys Langmuir adsorption isotherm and occurs spontaneously. The activation energy as well as other thermodynamic parameters obtained from their study revealed a strong interaction between the inhibitor molecules and mild steel surface. Electron impedance spectroscopy measurement result indicated that the resistance of the mild steel electrode increased greatly and its capacitance decreases by increasing the inhibitor concentration.

Thialagavathy and Saratha (2015) investigated the corrosion inhibition of mild steel in 1 M HCl using *Mirabilis Jalapa* flower extract at temperatures of 60^{o}C - 90^{o}C by weight loss and electrochemical method. Result of their study revealed that inhibition efficiency increased with increase in concentration of the extract as well as immersion period. Temperature studies indicated that inhibition efficiency increased up till 323 K and decreased with further increase in temperature. Potentiodynamic polarization result reveals a mixed type inhibitor. Experimental data obtained from their results fitted well with Langmuir and Temkin adsorption isotherm suggesting monolayer and physical adsorption

Saedah (2013) investigated the corrosion inhibition of mild steel in H_2SO_4 solution in the presence of Juniperus plant at the temperature ranges of 30^0C to 60^0C using weight loss, electrochemical (potentiodynamic polarization and Electron impedance spectroscopy) methods. His results revealed that inhibition efficiency increased with increase in inhibitor concentration but decreased with rise in temperature. The inhibitive effect of Juniperus plant was attributed to the presence of some compounds in the plant extract which is adsorbed on the surface of the mild steel. Experimental data obtained conformed well with Frumkin adsorption isotherm and Temkim adsorption isotherm at all concentration levels and temperatures studied. The phenomenon of physical adsorption process was proposed from activation parameters obtained. Thermodynamic parameters revealed that the adsorption was spontaneous.

Lebe *et al.* (2014) on the inhibition of mild steel in HCl solution by *Pentaclethra macrophlla Benytham* (PMB) extract in 1 M HCl using weight loss and electrochemical techniques (Open circuit potential, Linear sweep voltametry and potentiodynamic polarization) at 30 – 45^0C revealed that *Pentaclethra macrophylla Bentham* extract retarded the dissolution of mild steel in 1 M HCl solution. The inhibition efficiencies obtained increased with increase in extract concentration as well as increase in temperature which suggests physical and chemical adsorption mechanism. Open circuit potential shows reduction on resistance potential Rp with addition of the plant extract on the mild steel surface. Experimental data obtained fitted well with Langmuir and Temkin adsorption isotherm models. The mechanism of physisorption was proposed from the trend of inhibition efficiency with temperature obtained from experimental data.

Aijetha *et al.* (2015) carried out research work on the comparision of the corrosion inhibition efficiency of mild steel in different acidic media medium using *Commiphora Caudata* plant extract in 1 M HCl and H_2SO_4 medium using weight loss and electrochemical techniques. Results of their work revealed that inhibition efficiency varies with temperature and extract concentration. The corrosion inhibition behaviour of the extract was greater in HCl than in sulphuric acid. The adsorption of the inhibitor on the mild steel surface conformed with Langmuir adsorption isotherm. The inhibition efficiency increased as the temperature of the acid increased. Thermodynamic parameters obtained revealed that the adsorption of the inhibitor onto the mild steel was a spontaneous process and the polarization curve showed that the studied plant extract is a mixed type inhibitor in both acidic media

Bendahou *et al.* (2006), evaluated the effect of natural Rosemary oil as green inhibitor on the corrosion of steel in H_3PO_4 media at various temperatures. Various techniques were used including gravimetric and electrochemical methods to characterize the corrosion mechanism. Bedahou *et al.* (2006) demonstrated good agreement between the various method explored for corrosion inhibition analysis. The polarization measurement showed that Rosemary oil acted essentially as a cathodic inhibitor. The efficiency of corrosion inhibition of the oil increased with the concentration of extract to attain 73% at 10g/L but decreased with the rise in temperature from 25^oC to 73^0C range.

Abdel–Garber *et al* .(2008) studied the inhibition of Aluminum corrosion in 2 M sodium hydroxide solution in the presence and absence of 0.5 M NaCl using Damasissa (*Ambrosia Maritime,* L) extract employing different chemical and electrochemical techniques. Chemical gasometry techniques showed that addition of chloride or Damasissa extract to NaOH solution decreases the volume of hydrogen gas evolved suggested a decrease in metal corrosion. Potentiodynamic result manifested that chloride ions retard the anodic dissolution of aluminum below the pitting potential in NaOH solution. Damsissa extract in the presence and absence of chloride ions influenced both the anodic dissolution of aluminum and the generated hydrogen gas at the cathode indicating that the extract behaves as a mixed inhibitor. The decrease in the observed limiting current with increasing Damsissa extract concentration indicated that the anodic process is controlled by diffusion. The impedance result also showed that the Damsissa extract could serve as an effective inhibitor for corrosion of aluminum in alkaline solution. The impedance measurement verified the remarkable stability of the extract during storage up to 35 days. Damsissa extract was found more effective in the presence of chloride ions than in the absence. Inhibition was found to increase with increasing concentration of extract but decreases with increasing temperature .

Buchweishaya and Mhinzi (2008) investigated the inhibition effect of gum exudates from *Accia seyal var seyal* on corrosion of mild steel in drinking water using electrochemical techniques (ie potentiodynamic polarization and electrochemical impedance spectroscopy). The Acacia gum exudates are obtained from stems and branches of sub-saharan Legumino sae trees which grow extensively in central Tanzania. These exudates particularly from Senegal are permitted food additive (Anderson & Stoddart, 1996; Glicksman, 1983; JECFA/FAO, 1990). It was found that *Acacia Seyal var Seyal* could serve as an effective green corrosion inhibitor for mild steel in drinking water systems. The percentage inhibition efficiency was found to increase with increasing concentration of the gum, the inhibition efficiency was almost unaffected by the change of solution temperature.

The application of the extract of the leaves of *Citrus aurantifolia* plant on the corrosion inhibition of mild steel in 1M HCl solution was investigated using weight loss measurement and electrochemical studies (Saratha *et al.*, 2009). The result obtained showed that the extract served as an effective inhibitor for the corrosion protection of mild steel in 1 M HCl medium. The inhibitive action was discussed based on the adsorption isotherms and was found to fit all the model tested i.e Langmuir ,Temkin, Freundlish Frumkin and Flory-Huggins. The polarization curves revealed that this extract acts as a mixed type inhibitor. The author reported an inhibition efficiency of up to 97.5%.

Saratha and Vasudha (2009) investigated the acid extract of *Nyctanthes arbortristis* leaves on the corrosion inhibition of mild steel in aerated 1 M H_2SO_4 solution . The result indicated that the extract to be a good corrosion inhibitor. The phytoconsistuents of the leaves also contain mannitol, astringent principles, resinous tannic acid, flavanoids and iridoid glucosides (Saratha & Vasudha, 2009). The presence of this heterocyclic compounds enhanced the adsorption of this acid extract on the metal surface leading to effective inhibition of the mild steel corrosion in sulphuric acid. The maximum inhibition efficiency of about 90% was recorded at the inhibitor concentration of 1% v/v .

Kumar *et al.* (2003), have studied the alcoholic extract of leaves, latex and fruit from the *Calotropis gigantean* as corrosion inhibitors for mild steel in basic solution. The extract were reported to reduce the corrosion rate of mild steel in basic solution and gave up to 81% efficiency. The corrosion inhibition potential of *Calotropis procera* on mild steel in sulphuric acid medium was also tested by weight loss, electrochemical, SEM and UV methods. *Calotropis procera* was found to show significant corrosion inhibitive effect on mild steel in sulphuric acid medium (Raja & Sethuraman, 2009). Basically. calotropis is used as a traditional medicinal plant with unique properties to treat common diseases .

Uwah *et al.* (1981) investigated the corrosion inhibition performance of the ethanol extract of *Costus afer* stem (EECAS) on the corrosion of mild steel in 0.5 M HCl solution at temperatures of 303 K, 313 K, and 323 K. The experimental work was performed using weight loss (gravimetric) and hydrogen evolution (gasometric) technique. Their result revealed that the plant extract inhibited the corrosion of mild steel in acid medium and a maximum inhibition efficiency of 94.8% was observed at 5.0 g/l of costrus extract. Result of their study also showed that the inhibition efficiency increased with increase in concentration of the plant extract but decreases with rise in temperature. Adsorption of the extract on mild steel was found to obey Langmuir, Temkin, Frumkin and Freundlish adsorption isotherm.

Hamamou *et al.* (2012) investigated the inhibition effect of carob seed oil (CO) in C38 steel in 1 M HCl by weight loss and electrochemical measurement (potentiodynamic polarization). Result from their study revealed that the inhibition efficiency of castor oil depends on its concentration and attains approximately 86.7% at 0.5g/l. Polarization curves reveals that extract is a mixed type inhibitor. In addition, result obtained showed that the inhibition efficiency of the plant extract increased with decrease in temperature and adsorption of the extract on the C38 steel surface obeyed Langmuir adsorption isotherm. Carob fruit are widely used in boiled juice “pekmez” production and powder drink industry .Their seed are utilized in the food industry in the production of gum.

Ali and Folaud (2012) investigated the corrosion inhibition of ethanol extract of mulberry (*Morus nigral*) by weight loss, electrochemical polarization technique and hydrogen evolution measurement. The extract was found to be a good inhibitor for aluminum corrosion in acid solution. It was also discovered that the adsorption of the inhibitor is a spontaneous process and follows Langmuir adsorption isotherm. The inhibition efficiency (I.E) increased as the extract concentration increased and decreased with increase in temperature. The researchers also found that the extract provides a good protection to aluminum against pitting corrosion in chloride ion containing solution in corrosion of aluminum in 0.2 - 1.0 M H_2SO_4 solution by gravimetric technique. Result of their work showed that Newbouldia leaves is a good inhibitor in 1.0 M HCl than 0.5M H_2SO_4. It was observed that inhibition efficiency depends on the concentration of the plant extract as well as the time of exposure of aluminum samples in H_2SO_4 solution containing the extract. Experimental data complied to the Langmuir adsorption isotherm.

Cardozo *et al.* (2010) studied the inhibition effect of aqueous extract of mango, orange, passion fruit and cashew peels in 1 M HCl using electrochemical impedance spectroscopy, potentiodynamic polarization measurement, weight loss measurement and surface analysis. The inhibitors was found to be a mixed type and inhibition efficiency increased with increase in concentration of the extract. It was also observed that the adsorption of the inhibitor on the metal surface obeys Langmuir adsorption isotherm

Minaj *et al.* (1999) investigated the corrosion inhibition of Eucalyptus (leaves), Hibiscus (flower) and Agaricus on mild steel using weight loss (under static as well as dynamic conditions) and polarization method. Agaricus extract was found to be predominantly a cathodic inhibitor while the extract of Eucalyptus and Hibiscus were found to be a mixed inhibitors. The adsorption of the inhibitors obeyed Langmuir and Freunlish adsorption isotherm.

Odiongenyi *et al.* (2008), investigated the inhibitive and adsorption properties of ethanol extract of *Vernonia amygdalina* for the corrosion of mild steel in 0.2 - 0.5M H_2SO_4 at 303 K using weight loss, thermometric, gasometric and IR methods of monitoring corrosion. The result showed that the ethanol extract of *Vernonia amyadalina* inhibited the corrosion of mild steel. The inhibition efficiency increased as the concentration of the extract increases. The inhibitor was also found to be a mixed type inhibitor and the adsorption of the inhibitor followed

Langmuir adsorption isotherm. Phytochemical studies also revealed that ethanol extract of Vernonia amygdalina contains tannin, flavonoid and anthraquinone all contributing to the corrosion inhibition.

2.2. *Ocimum Gratissimum L.*

Ocimum gratissimum L. locally known as 'Nchanwu' belongs to the family Lamiaceae and is found mostly in the tropical countries such as Nigeria, North and South America, Mexico and Brazil. In Nigeria, it is locally known as Erumaba in Yoruba , Diadogatagida in Hausa and Nchanwu in Igbo. It is traditionally used to relief pains and in the treatment of rheumatism, diarrhea, high fever, convulsions, diabetes, eczema, piles and a repellant (Chitwood, 2003; Hotlets *et al.,* 2003; Pessoa *et al.,* 2003).

The phytochemical content of *Ocimum graissimum* L., are alkaloid, tannin, saponins, steroid, philobatanin,terpernoid, flavonoid and cardiacglycoside. (Akindahunsi & .Salawu, 2005).

Ocimum gratissimum L., can be characterized as follow:

Kingdom	Plantae
Subkingdom	Tracheobiont
Division	Magnolinophyta
Class	Magnoliopsida
Sub-class	Asteridae
Order	Lamiales
Family	Lamiaceae
Sub family	Nepetoideae

Tribe	Ocimeae
Gender	Ocimum
Species	O.gratissimum
Botanical name	*Ocimum gratissimum*
Common name	Nchanwu.

2.3. *Landolphia Heudelotii:*

It is locally known as 'Utokgbo', is a bushy or climbing shrub that produces stem up to 15 meters long The specie was used as main rubber supply in Senegal, Guinea and French Sudan (Modern Mali) (Dergal *et al.,*1999). The plant is found existing in western tropical African to Senegal, Nigeria and Ghana. It's habitat is mainly Savannah and understory shrub (Kamanzi, 2008). The plant grows under trees and promising for agro forestry , it is used to withstand bush fires and grazing .The pulp is edible, refreshing, slightly acidulous, mucilaginous and is known to promote good digestion (Glew *et al.,* 1997) .The plant is also rich in organic acids the pulp is used as a source of refreshing drink and also fermented to make alcoholic drink.

Medicinally the decoction of the stems or the roots is used for treating intestinal pains .The vapour from a boiling concoction of leafy twigs is inhaled orally for tooth troubles .The plant is used in draught and added to squat –baths in treating haemorrhoids. A decoction of the root and of the fruit pulp with some lime –juice is added to bath as a remedy for fatigue (Burkil, 2004).

The phytochemicals present in the plant are as follows carotenoids, anthraquinones,, flavonoids, anthocyanos, tannins, sterols-triterpenes and fibber (Cook *et al*., 2000)..

Landolphia heudelotii can be characterized as follows :

Kingdom	Plantae
Subkingdom	Tracheophyta
Division	Magnoliopsida
Class	Magnoliopsida –Dicotyledons
Subclass	Asteridae
Order	Gentianales
Family	Apocynaceae
Genus	Landolphia P.Beauv Landolphia
Species	Landolphia heudelotii
Botanical name	*Landolphia heudelotii*
Common name	Landolphia rubber
Local name	Utokgbo (Dresster *et al.*, 2014)

2.4 Some Phytochemical Component of *Landolphia Heudelotii and Ocimum gratissimum*.

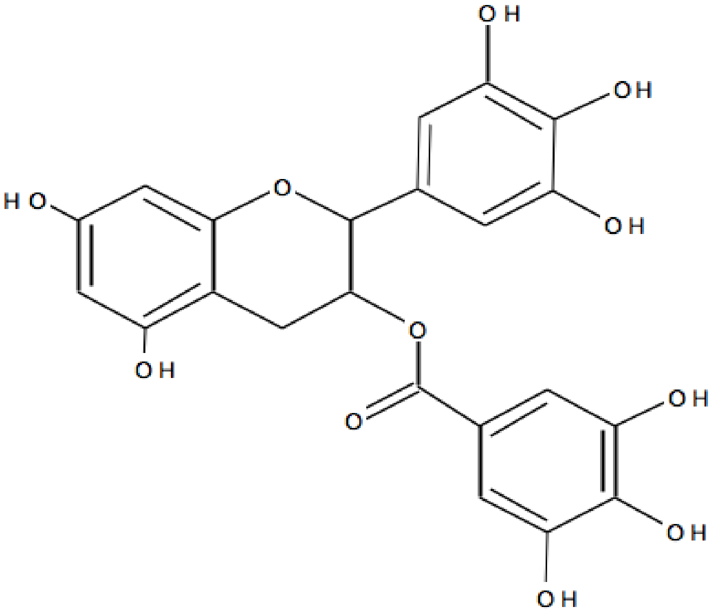

Figure 2.1. Tannin

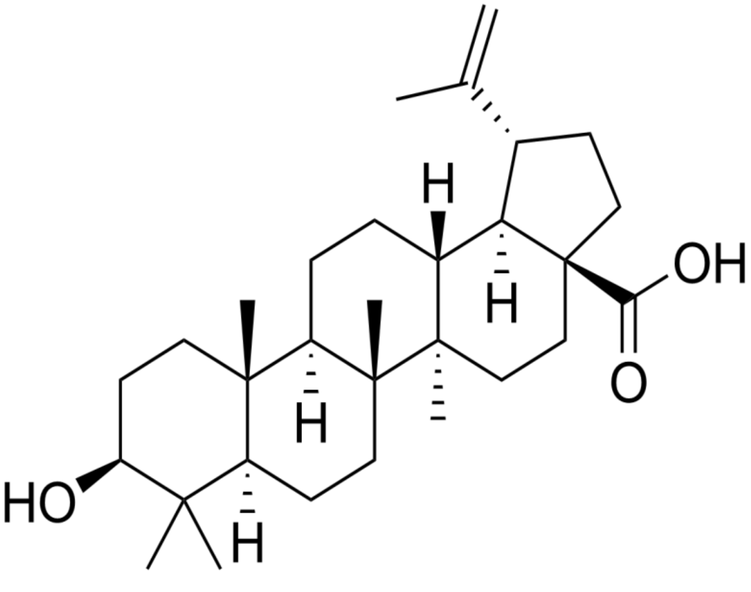

Figure 2.2: Triterpenes

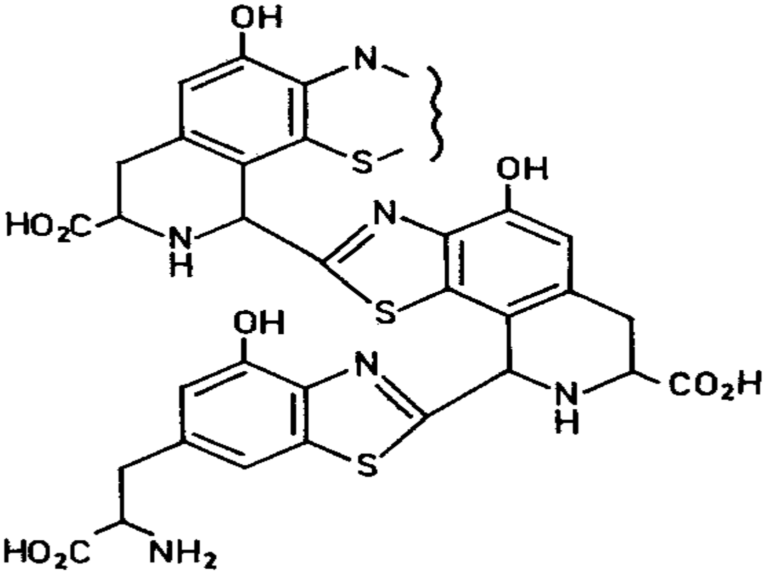

Figure 2.3: Structure of Carotenoids

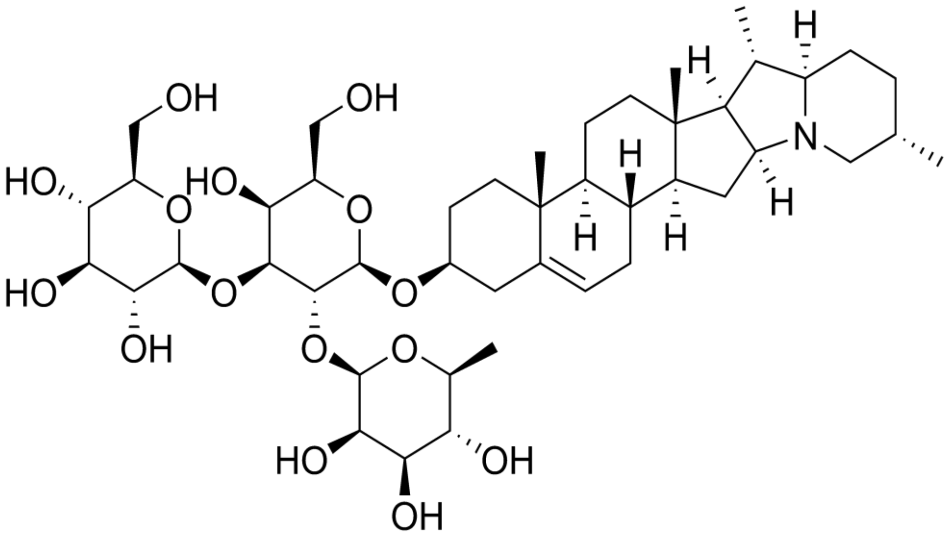

Figure 2.4: Saponins

CHAPTER THREE

MATERIALS AND METHOD

3.1 MATERIALS

Reagents

0.5 M H_2SO_4 solution

1 M HCl solution

Acetone

Ethanol

500ml Conical Flask Beakers

2000ml round bottom flask

1000ml volumetric flask

Reflux condenser

50ml measuring cyclinder

100ml measuring cylinder

Water bath

Retort stand

Wire gauze

Electronic digital weighing balance.

Ground Utokgbo leaves *(Landolphia heudelotii*)

Ground Nchanwu Leaves *(Ocimum gratissimum)*

3.2 Material Preparation

The sheets of mild steel used for this experiment has the following composition: carbon 0.05, Silicon 0.3, Manganese 0.6, Phosphorous 0.36, the rest iron. The sheets were obtained from materials and metallurgical engineering workshop, Federal University of Technology Owerri. The sheets were mechanically press cut into 30cm by 30cm samples These sheets were polished using different grades of emery papers, degreased in ethanol, dried in acetone and electrical hand drier before storing in a moisture free desiccators prior to use (Ebenso *et al.,* 2008; Okarfor *et* al., 2007; Oguzie, 2008; Uwah *et al.,* 2013). The aggressive solution used were 1 M HCl and 0.5 M H_2SO_4 and were prepared by dilution of concentrated hydrochloric and sulphuric acid with distilled water and experiment were carried out in unstirred solution and all weighing were done using electronic digital weighing balance.

Figure 3.1 : Coupons used for weight loss analysis.

3.3 Preparation of Extracts from *Landolphia heudelotii and Ocimum gratissimum*

The leaves of *Landolphia heudelotii* and *Ocimum gratissimum* were collected from a local bush in Avu village in Owerri West Local Government Imo State and identified at the Department of Agriculture and Technology, Federal university of Technology Owerri. They were washed with distilled water dried at room temperature to avoid loss of major organic component of the plant and ground to powdered form. 40g of the powdered samples were weighed respectively using electronic weighing balance and each were extracted using solvent extraction by refluxing for 3 hours with a reflux condenser at a temperature range of 30 to 40^{o}C . The concentrations of the extracts were calculated. From the stock solution, inhibition test solution were prepared to obtain 500mg/l, 1000mg/l, 1500mg/l, 2000mg/l and 2500mg/l used for weight loss measurement.

3.4 Preparation of Environment

Six different environments were used for the study namely:

0.5M H_2SO4

1M HCl,

0.5M H_2SO_4 + *Landolphia heudelotii,*

0.5M H_2SO_4 + *Ocimum gratissimum*

1M HCl + *Ocimum gratissimum*

1M HCl + *Landolphia heudelotii*.

Figure 3.2 Different prepared corrosive environment used for weight loss analysis.

3.5 Experimental Set- Up and Monitoring

3.51. Weight loss measurement:

Corrosion rates and inhibition efficiency were monitored using weight loss technique. The initial weight of the coupons were recorded to the nearest 0.0000 using electronic digital weighing balance. The coupons were totally immersed in a 300ml beakers with the aid of a glass rod and a hook containing different prepared environment. The procedure was conducted with and without the various concentration of the plant extract after which the various coupons were withdrawn from the corrosive environment, cleaned with ethanol, before drying using acetone and electronic hand drier and then reweighed . The weight loss was taken as the difference in weight of the specimen before and after immersion. The experiment was conducted in duplicate to ensure reliability of the result and the mean weight loss was reported. (Oguzie, 2006; Okafor *et al.*,2012; Uwah *et al.*, 2012). .

The corrosion rate and inhibition efficiency is given by the equation

Corrosion rate = $\frac{Weight\ loss\ (\Delta W)}{Area\ \times Time}$ (9)

$$CR = \frac{\Delta W}{AT}$$

ΔW = Weight loss in grams

A = Area of coupon in cm^2

T = Time in hours

Inhibition efficiency (I.E) = $1 - \frac{W_{inh}}{W_{blk}} \times 100$ (10)

Where W_{inh} = weight loss in inhibitor

W_{blk} = weight loss in blank

3.6 Temperature Studies

Temperature studies were carried out by immersing pre- weighed coupons in 300ml beakers each of blank 1 M HCl and 0.5 M H_2SO_4 and the test solutions of two different concentration (highest and lowest) at 313 K, 323 K and 333 K in a thermostat controlled water bath for three hours . The specimen were taken out, air dried and re- weighed. From the study, the weight loss, inhibition efficiency and corrosion rate were determined by applying the mathematical model stated in equation **9** and **10** above. Thermodynamic parameters were also obtained from experimental data. The activation energy of adsorption process was calculated using Arrhenius equation stated as follows

$$\ln \frac{CR_2}{CR_1} = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (11)$$

where CR_1 and CR_2 are corrosion rates at T_1 and T_2 respectively, Ea is the activation energy of reaction and R is the rate constant.

Gibb's free energy of reaction was also calculated using the relationship between equilibrium constant of the adsorption (K_{ads}) of water extract of *Landolphi heudelotii* and *Ocimum gratissimum* and the Gibb's free energy stated as follows

$$\Delta G = -2.303\ RT\ \mathrm{Log}\ (55.5K_{ads.}) \qquad (12)$$

Where K_{ads} the adsorption constant expressed as follows : $K_{ads} = \frac{\theta}{C_{inh}(1-\theta)}$

Where θ is the degree of surface coverage obtained from Langmuir adsorption isotherm, C_{inh} is the various concentration of the inhibitors , T is the temperature, R is the rate constant and 55.5 is constant for the molar heat of adsorption of water in solution.

The energy of adsorption which is approximately equal to enthalpy change or change in heat content of reaction is obtained using the trend in degree of surface coverage with rise in temperature expressed as follows

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta}{1-\theta_2}\right) - \log\left(\frac{\theta}{1-\theta_1}\right)\right] \times \frac{T_1T_2}{T_2-T_1} \qquad (13)$$

Where θ_1 and θ_2 are the degree of surface coverage at temperature T_1 and T_2 and R is the rate constant.

3.7 Electrochemical Measurement

Electrochemical testing of inhibitors has the major benefit of short measurement time and provides vital information on the mechanism of inhibition. The electrochemical cell used is a conventional three cell electrode Pyrex glass cell. The mild steel specimen used was embedded in Teflon holder using epoxy resin with exposed area of 1cm^2. A graphite rod was used as counter electrode, the reference electrode was a saturated calomel Electrode (SCE) coupled in a luggin capillary whose tip was located between the working and auxiliary electrode .Electrochemical measurement were run using a potentiostat/galvonostat 263 electrochemical system with a potential range of ± 250mVs^{-1} vs an open circuit potential (OCP) at a scan rate of 0.333mVs^{-1} . The measurement was run for the highest, lowest and blank solution of both inhibitor in two different corrosive media (1 M HCl and 0.5 M H_2SO_4). Prior to the experiment the working electrode was polished successfully with different grades of emery papers and then the polished metal surface was rinsed with de-ionised water, ethanol, dried with acetone and finally dipped in the test solution . A time interval of 10 minutes was allowed for each experiment to reach an open circuit potential . The measurement was carried out in the frequency range of 10^6 - 10^{-2} Hz at the open circuit potential by super imposing a sinusoidal AC signal of small amplitude of 10 mV. The data acquisition was performed and analyzed using the power suite (version 3.21) to evaluate the corrosion kinetics parameter such as corrosion current density (I_{corrr}), corrosion potential (E_{corr}), Tafel slopes b_a and b_c . (Kumaravel *et al.,* 2011; Oguzie, 2006; Loto, 2011).

From the polarization curves, tafel slopes, corrosion potential and corrosion current were analyzed using computer software (Ashassi – Sorkhabi and Seifzadeh, 2006). The inhibition efficiency was calculated using Tafel method according to the equation below:

$$\text{Inhibition Efficiency (\%)} = \frac{I_{corr\ (blank\ )} - I_{corr\ (inh)}}{I_{corr\ (blank\ )}} \qquad (14)$$

Where

I_{corr}(blank) = corrosion current density without inhibitor

I_{Corr}(inh) = corrosion current density with inhibitor.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 RESULTS

Tables 4.1 – 4.2.8 below reveals results of weight loss analysis on the corrosion inhibition of mild steel using *Landolphia heudelotii* and *Ocimum gratissimum* in 1 M HCl and 0.5 M H_2SO_4 at different immersion period showing the corrosion rate and inhibition efficiencies obtained after each analysis.

TABLE 4.1: Weight loss(g), corrosion rate (gcm^{2}hr) and inhibition efficiency(%) values for mild steel corrosion in 1 M HCl with and without water extract of LH after 3 hours .

System	Initial Weight (g)	Final Weight (g)	Weight Loss (g)	Average Weight Loss(g)	Area of Coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.5795	3.5647	0.0148	0.01825	0.16714	0.8732	---------
B	3.5795	3.5579	0.0217				
500mg/L	3.4168	3.4035	0.0133	0.01465	0.16714	0.7012	19.72
	3.5974	3.5814	0.0160				
1000mg/L							
A	3.4344	3.4249	0.0095	0.01305	0.16714	0.6246	28.49
B	3.5036	3.4870	0.0166				
1500mg/L							
A	3.5290	3.5198	0.0092	0.0098	0.16714	0.4691	46.30
B	3.4260	3.4156	0.0104				
2000mg/l							
A	4.5418	4.5323	0.0095	0.00526	0.16714	0.2518	71.18
B	5.0132.	5.0030	0.0010				
2500mg/l							
A	4.7283	4.7236	0.0047	0.0035	0.16714	0.1675	80.82
B	5.0914	5.0891	0.0023				

Table 4.2: Weight lossI(g), corrosion rate (g/cm^{2}hr), inhibition efficiency(%) values of mild steel corrosion in 1 M HCl with and without water Extract of OG after 3 hours.

System	Initial Weight(g)	Final Weight(g)	Weight loss(g)	Average weight Loss(g)	Area of coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency (%)
Blank							
A	3.4062	3.3902	0.0160	0.01665	0.16714	0.7969	------
B	3.3202	3.3029	0.0173				
500mg/L							
A	3.6288	3.6152	0.0136	0.01265	0.16714	0.6055	24.02
B	3.3039	3.2922	0.0117				
1000mg/L							
A	3.3245	3.3143	0.0102	0.01075	0.16714	0.5145	35.46
B	3.4922	3.4809	0.0113				
1500mg/L							
A	3.5121	3.5021	0.0100	0.01015	0.16714	0.4858	39.04
B	3.3290	3.3187	0.0103				
2000mg/l							
A	4.5955	4.5875	0.0080	0.0076	0.16714	0.3638	54.35
B	4.7898	4.7826	0.0072				
2500mg/l							
A	4.8592	4.8546	0.0046				
B	4.8343	4.8287	0.0056	0.0051	0.16714	0.2441	69.37

Table 4.3: Weight loss(g), corrosion rate (g/cm^{2}hr), inhibition efficiency(%) values of mild steel corrosion in 0.5 M H_2SO_4 with and without water extract of LH after 3 hours

System	Initial Weight(g)	Final Weight(g)	Weight Loss(g)	Average Weight Loss(g)	Area of Coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency (%)
Blank							
A	3.4579	3.4347	0.0232	0.02565	0.16714	1.2277	-----
B	3.6062	3.5781	0.0281				
500mg/L							
A	3.6234	3.5970	0.0264	0.0237	0.16714	1.1344	7.60
B	3.3622	3.3412	0.0210				
1000mg/L							
A	3.4340	3.4073	0.0267	0.0232	0.16714	1.1104	9.55
B	3.5124	3.4927	0.0197				
1500mg/L							
A	3.5290	3.5241	0.0149	0.01465	0.16714	0.7012	42.88
B	3.3296	3.3152	0.0144				
2000mg/l							
A	5.0614	5.0489	0.0125	0.0122	0.16714	0.5840	52.44
B	4.5821	4.5702	0.0119				
2500mg/l							
A	4.9462	4.9362	0.0100	0.009	0.16714	0.4308	64.91
B	5.0166	5.0086	0.0080				

Table 4.4: Weight loss(g) , corrosion rate (g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 0.5 M H_2SO_4 with and without extract of OG after 3hours .

System	Initial Weight (g)	Final Weight (g)	Weight loss(g)	Average weight loss (g)	Area of Coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency
Blank							
A	3.2756	3.2529	0.0227	0.0275	0.16714	1.3163	--------
B	3.6970	3.6647	0.0323				
500mg/L A							
B	3.4358	3.4236	0.0122	0.0232	0.16714	1.1104	15.64
	3.5767	3.5425	0.0342				
1000mg/L							
A	3.1921	3.1830	0.0091	0.00915	0.16714	0.4379	66.72
B	3.3893	3.3801	0.0092				
1500mg/L							
A	3.5863	3.5765	0.0098	0.00885	0.16714	0.4326	67.82
B	3.2277	3.2198	0.0079				
2000mg/l							
A							
B	4.7265	4.7200	0.0065	0.0058	0.16714	0.2776	78.91
	4.8650	4.8599	0.0051				
2500mg/l							
A	4.8517	4.8467	0.0050	0.0053	0.16714	0.2537	80.72
B	4.9584	4.9528	0.0056				

Table 4.5: Weight loss(g), corrosion rate (g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 1 M HCl with and without water extract of LH after (six) 6 hours

System	Initial Weight(g)	Final Weight(g)	Weight Loss(g)	Average Weight Loss(g)	Area of coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.5259	3.5030	0.0229	0.0212	0.16714	0.5074	--------
B	3.3432	3.3237	0.0195				
500mg/L							
A	3.2106	3.1906	0.0200	0.0187	0.16714	0.4475	11.79
B	3.3923	3.2749	0.0174				
1000mg/L							
A	3.3835	3.3692	0.0143	0.0140	0.16714	0.3350	33.96
B	3.5074	3.4937	0.0137				
1500mg/L							
A	3.3099	3.2971	0.0128	0.01305	0.16714	0.3123	38.44
B	3.4131	3.3998	0.0133				
2000mg/l	4.7071						
A	4.0391		0.0114	0.01075	0.16714	0.2573	49.29
B			0.0101				
2500mg/l							
A	4.1071		0.0088	0.0076	0.16714	0.1819	64.15
B	4.5551		0.0064				

Table 4.6: Weight loss(g), corrosion rate (g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 1 M HCl with and without water extract of OG after(six) 6 hours.

System	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight loss(g)	Area of coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.2378	3.2092	0.0286	0.02855	0.16714	0.6833	------
B	3.4048	3.3763	0.0285				
500mg/L							
A	3.1873	3.1683	0.0190	0.0175	0.16714	0.4188	38.70
B	3.3254	3.3094	0.0160				
1000mg/L							
A	3.3830	3.3672	0.0158	0.0136	0.16714	0.3247	52.36
B	3.5353	3.5239	0.0114				
1500mg/L							
A	4.5199		0.0112	0.0109	0.16714	0.2609	61.82
B	4.8405		0.0106				
2000mg/l							
A	3.3697	3.3637	0.0060	0.0055	0.16714	0.1316	80.74
B	3.4072	3.4020	0.0052				
2500mg/l							
A	4.8851	4.8808	0.0043	0.0046	0.16714	0.1101	83.89
B	4.7375	4.7326	0.0049				

Table 4.7: Weight loss(g), corrosion rate(g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 0.5 M H_2S0_4 with and without water extract of LH after (six) 6 hours.

System	Initial Weight (g)	Final Weight (g)	Weight loss(g)	Average Weight loss(g)	Area of coupon (g)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency (%)
Blank							
A	3.4403	3.3959	0.0444	0.0472	0.16714	1.1296	-------
B	3.4485	3.3985	0.0500				
500mg/L							
A	3.1907	3.1649	0.0258	0.02775	0.16714	0.6641	41.21
B	3.3794	3.3497	0.0297				
1000mg/L							
A	3.6043	3.5811	0.0232	0.02115	0.16714	0.5062	55.19
B	3.3230	3.3039	0.0191				
1500mg/L							
A	3.6505	3.6326	0.0179	0.0179	0.16714	0.4284	62.08
B	3.3782	3.3603	0.0179				
2000mg/l							
A							
B	4.9386	4.9223	0.0163	0.0161	0.16714	0.3853	65.88
	4.5953	4.5824	0.0159				
2500mg/l							
A	4.6444	4.6302	0.0142	0.0140	0.16714	0.3350	70.34
B	4.8583	4.8445	0.0138				

Table 4.8: Weight loss(g), corrosion rate(g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 0.5 M H_2SO_4 with and without water extract of OG after(six) 6 hours.

System	Initial weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight loss(g)	Area of coupon (cm^2)	Corrosion rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.2988	3.2466	0.0522	0.0559	0.161714	1.3378	--------
B	3.5017	3.4421	0.0596				
500mg/L							
A	3.3392	3.3234	0.0158	0.01535	0.161714	0.3674	72.54
B	3.5184	3.5035	0.0149				
1000mg/L							
A	3.4304	3.4147	0.0157	0.0147	0.161714	0.3518	73.70
B	3.5237	3.5100	0.0137				
1500mg/L							
A	3.4211	3.4099	0.0112	0.0134	0.161714	0.3207	76.02
B	3.5836	3.5680	0.0156				
2000mg/l							
A	4.5600	4.5499	0.0101	0.0105	0.16714	0.2513	81.22
B	4.8383	4.8274	0.0109				
2500mg/l							
A							
B	4.8820	4.8725	0.0095	0.00875	0.16714	0.2094	84.35
	4.8683	4.8603	0.0080				

Table 4.9: Weight loss(g), corrosion rate(g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 1 M HCl with andwithout water extract of LH after 24 hours

System	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight Loss (g)	Area of Coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency (%)
Blank							
A	3.3455	3.0440	0.3015	0.3214	0.16714	1.9229	-------
B	3.3945	3.0532	0.3413				
500mg/L							
A	3.3135	3.1714	0.1421	0.1293	0.16714	0.7736	59.77
B	3.3206	3.2041	0.1165				
1000mg/L							
A	3.4061	3.3061	0.1000	0.1000	0.16714	0.5983	68.89
B	3.5179	3.4179	0.1000				
1500mg/L							
A	3.3146	3.24883	0.0658	0.0705	0.16714	0.4218	78.06
B	3.4050	3.3298	0.0752				
2000mg/l							
A	3.5012	3.4512	0.0500	0.0652	0.16714	0.3901	80.55
B	3.2360	3.1556	0.0804				
2500mg/l							
A	3.5700		0.0453	0.0510	0.16714	0.3051	84.13
B	3.2397		0.0567				

Table 4.10 Weight loss(g), corrosion rate(g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 1 M HCl with and without water extract of OG after 24 Hours

System	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight Loss(g)	Area of Coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.4682	3.0082	0.4100	0.4582	0.16714	2.7414	-------
B	3.5489	3.0416	0.5064				
500mg/L							
A	3.2632	3.1632	0.1000	0.1025	0.16714	0.6133	77.63
B	3.2323	3.1273	0.1050				
1000mg/L							
A	3.4176	3.3188	0.0988	0.0944	0.16714	0.5648	79.40
B	3.4377	3.3477	0.0900				
1500mg/L							
A	3.1967	3.1123	0.0844	0.0821	0.16714	0.4912	82.08
B	3.4979	3.4181	0.0798				
2000mg/l							
A	3.4112	3.4945	0.0833	0.0765	0.16714	0.4577	83.30
B	3.5343	3.6039	0.0696				
2500mg/l							
A	3.3137	3.2687	0.0450	0.0413	0.16714	0.2471	88.80
B	3.3403	3.3027	0.0376				

Table 4.11: Weight loss(g), corrosion rate(g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 0.5 M H_2SO_4 with and without water extract of LH after 24 hours

System	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight Loss(g)	Area of Coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.4329	3.4038	0.0928	0.10335	0.16714	0.6183	------
B	3.5109	3.3333	0.1139				
500mg/L							
A	3.4180	3.4073	0.0107	0.0386	0.16714	0.2309	62.65
B	3.4458	3.3793	0.0665				
1000mg/L							
A	3.3005	3.2793	0.0212	0.0264	0.16714	0.1580	74.45
B	3.2993	3.2677	0.0316				
1500mg/L							
A	3.4027	3.3829	0.0198	0.021	0.16714	0.1256	79.68
B	3.4807	3.4585	0.0222				
2000mg/l							
A							
B	3.3305	3.3130	0.0175	0.01795	0.16714	0.1074	82.63
	3.5041	3.4857	0.0184				
2500mg/l							
A	3.4133	3.4019	0.0114	0.0129	0.16714	0.0772	87.52
B	3.4883	3.4739	0.0144				

Table 4.12: Weight loss(g), corrosion rate(g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 0.5 M H_2SO_4 with and without water extract of OG after 24hours

System	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight Loss(g)	Area of Coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.4884	3.3008	0.1876	0.18235	0.16714	1.0910	-------
B	3.4336	3.2565	0.1771				
500mg/L							
A	3.3573	3.2909	0.0664	0.0680	0.16714	0.4068	62.70
B	3.6093	3.5397	0.0696				
1000mg/L							
A	3.2361	3.1920	0.0441	0.0455	0.16714	0.2722	75.05
B	3.5638	3.5169	0.0469				
1500mg/L							
A	3.4248	3.4018	0.0230	0.02160	0.16714	0.1292	88.15
B	3.2518	3,2296	0.0222				
2000mg/l							
A	3.2337	3.2215	0.0122	0.01745	0.16714	0.1044	90.40
B	3.6356	3.6129	0.0227				
2500mg/l							
A	3.5354	3.5188	0.0166	0.01575	0.16714	0.0942	91.36
B	3.4182	3.4033	0.0149				

Table 4.13: Weight loss(g), corrosion rate(g/cm^{2}hr) and inhibition efficiency(%) values of mild steel in 1 M HCl with and without water extract of LH after 72 hours

System	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight Loss(g)	Area of coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.0852	2.8753	0.2099	0.21055	0.16714	0.4199	-------
B	3.5340	3.3228	0.2112				
500mg/L							
A	3.5010	3.4339	0.0671	0.0693	0.16714	0.1382	67.09
B	3.3439	3.2724	0.0715				
1000mg/L							
A	3.1974	3.1325	0.0649	0.06885	0.16714	0.1373	67.30
B	3.5529	3.4801	0.0728				
1500mg/L							
A	3.3877	3.3178	0.0699	0.06755	0,16714	0.1347	67.92
B	3.4862	3.4210	0.0652				
2000mg/l							
A	4.6590	4.5960	0.0632	0.0630	0.16714	0.1256	70.78
B	4.6794	4.6166	0.0628				
2500mg/l							
A	4.9480	4.8906	0.0574	0.0586	0.16714	0.1169	72.16
B	4.8914	4.8316	0.0598				

Table 4.14: Weight loss(g), corrosion rate(g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 1 M HCl with and without water Extract of OG after 72 hours

System	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight Loss(g)	Area of Coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency
Blank							
A	3.3466	3.1918	0.1548	0.16275	0.16714	0.3246	------
B	3.4383	3.2676	0.1707				
500mg/L							
A	3.4413	3.3865	0.0548	0.05965	0.16714	0.1190	63.35
B	3.4960	3.4315	0.0645				
1000mg/L							
A	3.4423	3.3979	0.0444	0.04470	0.16714	0.0891	72.53
B	3.5517	3.5067	0.0450				
1500mg/L							
A	3.4142	3.4142	0.0452	0.04010	0.16714	0.0800	75.36
B	3.4288	3.4288	0.0350				
2000mg/l							
A	3.3797	3.3529	0.0268	0.0325	0.16714	0.0648	80.00
B	3.3432	3.3049	0.0383				
2500mg/l							
A	3.4550	3.4355	0.0195	0.0016	0.16714	0.00319	88.47
B	3.4196	3.3559	0.0637				

Table 4.15: Weight loss(g), corrosion rate (g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 0.5 M H_2SO_4 with and without water extract of LH after 72 hours

System	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight Loss(g)	Area of Coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.5075	1.8500	1.6575	1.5637	0.16714	3.1185	-------
B	3.5669	2.0970	1.4699				
500mg/L							
A	4.7963	4.2984	0.4979	0.49415	0.16714	0.9856	68.40
B	5.0932	4.6024	0.4904				
1000mg/L							
A	48908	4.5554	0.3354	0.3439	0.16714	0.6859	78.00
B	4.7936	4.8532	0.3524				
!500mg/L							
A	3.4225	3.1143	0.3082	0.3277	0.16714	0.6535	79.58
B	3.4720	3.1248	0.3472				
2000mgl							
A	3.3602	3.0980	0.2622	0.26005	0.16714	0.5186	83.37
B	3.5199	3.2620	0.2579				
2500mg/l							
A	3.3464	3.2161	0.1303	0.1625	0.16714	0.3241	89.61
B	3.3639	3.1692	0.1947				

Table 4.16: Weight loss(g), corrosion rate (g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 0.5 M H_2SO_4 with and without water extract of OG after 72 hours

System	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight Loss(g)	Area of Coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.0776	1.8041	1.2735	1.2893	0.16714	2.5713	------
B	3.3891	3.0998	1.2893				
500mg/L							
A	3.2055	2.9213	0.2842	0.2610	0.16714	0.5205	79.76
B	3.8760	3.1382	0.2378				
1000mg/L							
A	3.4917	3.2371	0.2546	0.2449	0.16714	0.4884	80.89
B	3.2737	3.0385	0.2352				
1500mg/l							
A	3.1825	3.0134	0.1691	0.1959	0.16714	0.3906	84.81
B	3.4175	3.1948	0.2227				
2000mg/L							
A	3.3093	3.1390	0.1703	0.1755	0.16714	0.3500	86.30
B	3.5185	3.3378	0.1807				
2500mg/L							
A	3.2539	3.1781	0.0758	0.0768	0.16714	0.1531	94.00
B	3.4703	3.3925	0.0778				

Table 4.17: Weight loss(g), corrosion rate (g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 1 M HCl with and without water extract of LH after 72 hours

System	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight Loss(g)	Area of coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency (%)
Blank							
A	3.4867	3.0993	0.3874	0.3654	0.16714	0.3644	------
B	3.2446	2.9012	0.3434				
500mg/L							
A	3.4652	3.3484	0.1168	0.1042	0.16714	0.1039	71.48
B	3.5944	3.5028	0.0916				
1000mg/L							
A	3.6051	3.5102	0.0949	0.09135	0.16714	0.0911	75.00
B	3.2694	3.1816	0.0878				
1500mg/L							
A	3.2527	3.1547	0.0835	0.0825	0.16714	0.0823	77.49
B	3.3665	3.2676	0.0810				
2000mg/l							
A	4.8082	4.7339	0.0743	0.0683	0.16714	0.0681	81.32
B	4.9830	4.9208	0.0622				
2500mg/l							
A	5.0744	5.0151	0.0587	0.0589	0.16714	0.00587	83.88
B	4.7460	4.6868	0.0592				

Table 4.18: Weight loss(g), corrosion rate (g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 1 M HCl with and without extract of OG after 144 hours.

System	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight Loss(g)	Area of Coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.4482	2.9964	0.4516	0.4572	0.16714	0.4559	-------
B	3.5360	3.0734	0.4626				
500mg/L							
A	3.3717	3.2971	0.0746	0.0798	0.16714	0.0796	82.55
B	3.4347	3.3497	0.0850				
1000mg/L							
A	3.5546	3.4921	0.0625	0.0610	0.16714	0.0608	86.66
B	3.1266	3.0671	0.0595				
1500mg/L							
A	3.3761	3.3270	0.0496	0.0525	0.16714	0.0523	88.52
B	3.2793	3.2234	0.0559				
2000mg/l							
A							
B	3.5594	3.5190	0.0404	0.0408	0.16714	0.0406	91.08
	3.4577	3.4165	0.0412				
2500mg/l							
A	3.2366	3.2007	0.0359	0.03475	0.16714	0.03465	92.40
B	32336	3.200	0.0336				

Table 4.19: Weight loss(g), corrosion rate(g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 0.5 M H_2SO_4 with and without water extract of LH after 144 hours

System	Initial Weight(g)	Final Weight(g)	Weight Loss(g)	Average Weight Loss(g)	Area of Coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.4095	1.1276	2.2819	2.3273	0.16714	2.3207	--------
B	3.4939	1.1212	2.3727				
500mg/L							
A	3.6954	2.9612	0.7342	0.7355	0.16714	0.7334	68.40
B	3.3912	2.6544	0.7368				
1000mg/L							
A	3.4230	2.8126	0.6104	0.6017	0.16714	0.6000	74.14
B	3.3341	2.7410	0.5931				
1500mg/l							
A	4.9866	4.3769	0.6097	0.56755	0.16714	0.5659	75.13
B	4.5218	3.9964	0.5254				
2000mg/l							
A	5.0591	4.4964	0.5627	0.5349	0.16714	0.5333	77.01
B	5.1261	4.5390	0.5071				
2500mg/l							
A	3.5606	3.1338	0.4268	0.4082	0.16714	0.4070	82.46
B	3.1208	2.7312	0.3896				

Table 4.20: Weight loss(g), corrosion rate(g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 0.5 M H_2SO_4 with andwithout water extract of OG after 144 hours.

System	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight Loss(g)	Area of Coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.3073	1.5990	1.7083	1.7366	0.16714	1.7317	-------
B	3.4553	1.6903	1.7650				
500mg/L							
A	3.4848	3.1537	0.3311	0.3401	0.16714	0.3391	80.42
B	3.3036	2.9545	0.3491				
1000mg/L							
A	3.4048	3.1246	0.2802	0.2893	0.16714	0.2884	83.34
B	3.4626	3.1642	0.2984				
1500mg/L							
A	3.3677	3.1408	0.2269	0.2253	0.16714	0.2247	87.03
B	3.2862	3.0625	0.2237				
2000mg/l							
A							
B	3.3305	3.2042	0.1263	0.11985	0.16714	0.1195	89.76
	3.4639	3.3505	0.1134				
2500mg/l							
A	3.4337	3.3566	0.0771	0.0787	0.16714	0.0785	95.47
B	3.4138	3.2432	0.0804				

Table 4.21 : Weight loss(g), corrosion rate(g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 1 M HCl with and without water Extract of LH after 216 hours.

System	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight Loss(g)	Area of Coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.3008	2.5839	0.7169	0.76995	0.16714	0.5118	-------
B	3.4626	2.6396	0.8230				
500mg/L							
A	3.4605	3.2502	0.2103	0.2150	0.16714	0.1429	72.08
B	3.6195	3.3998	0.2197				
1000mg/L							
A	3.5855	3.4359	0.1496	0.1351	0.16714	0.0898	82.45
B	3.5736	3.4530	0.1206				
1500mg/L							
A	3.4348	3.3472	0.0876	0.0641	0.16714	0.0426	91.68
B	3.3119	3.2714	0.0405				
2000mg/l							
A	4.6757	4.6232	0.0525	0.0553	0.16714	0.0368	92.82
B	4.5860	4.5279	0.0581				
2500mg/L							
A	4.4215	4.3703	0.0512	0.0508	0.16714	0.0338	93.40
B	4.7875	4.7371	0.0504				

Table 4.22 : Weight loss(g), corrosion rate(g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion 1 M HCl with and without water extract of OG after 216 hours.

System	Initial Weight (g)	Final Weight Loss(g)	Weight Loss(g)	Average Weight Loss(g)	Area of Coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency
Blank							
A	3.4466	2.7302	0.7164	0.72205	0.16714	0.4800	-------
B	3.4096	2.6819	0.7277				
500mg/L							
A	3.6492	3.5354	0.1138	0.11015	0.16714	0.0732	84.74
B	3.5536	3.4471	0.1065				
1000mg/L							
A	3.2545	3.1703	0.0842	0.0779	0.16714	0.0518	89.21
B	3.3078	3.2362	0.0716				
1500mg/L							
A	3.4124	3.3924	0.0200	0.03275	0.16714	0.0217	95.46
B	3.5147	3.4692	0.0455				
2000mg/l							
A							
B	3.5119	3.4813	0.0306	0.0313	0.16714	0.0151	95.66
	3.4823	3.4511	0.0312				
2500mg/l							
A	4.5052	4.4772	0.0280	0.02825	0.16714	0.0109	96.09
B	4.4952	4.4667	0.0285				

Table 4. 23 : Weight loss(g), corrosion rate(g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 0.5 M H_2SO_4 with and without water extract of LH after 216 hours.

System	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight Loss(g)	Area of Coupon (cm^2)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.5059	0.0468	3.4591	3.3693	0.16714	2.2398	**-----**
B	3.3264	0.0468	3.2796				
500mg/L							
A	5.0298	3.8724	1.1574	1.1928	0.16714	0.7929	64.60
B	4.9571	3.7289	1.2282				
1000mg/L							
A	3.1110	2.0900	1.0210	1.09035	0.16714	0.7248	67.64
B	3.2908	2.1311	1.1597				
1500m/L							
A	4.8761	3.8545	1.0221	0.97655	0.16714	0.6488	71.00
B	4.6943	3.7633	0.9310				
2000mg/l							
A							
B	3.4331	2.5368	0.8963	0.9035	0.16714	0.6006	73.18
	3.3616	2.4309	0.9107				
2500mg/l							
A	3.3782	2.5929	0.7853	0.7727	0.16714	0.5137	77.07
B	3.1871	2.4269	0.7602				

Table 4. 24: Weight loss(g), corrosion rate(g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 0.5 M H_2SO_4 with and without water extract of OG after 216 hours.

System	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight Loss	Area of Coupon Cm^2	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.4947	0.1742	3.3205	3.2578	0.16714	2.1657	------
B	3.3693	0.1742	3.1951				
500mg/L							
A	5.2892	2.7200	0.7233	0.66895	0.16714	0.4447	79.46
B	4.6583	3.4138	0.6146				
1000mg/L							
A	3.4945	2.9708	0.5237	0.54945	0.16714	0.3653	83.13
B	3.5973	3.0221	0.5752				
1500mg/L							
A	3.2516	2.8442	0.4090	0.4296	0.16714	0.2856	86.81
B	3.5029	3.0527	0.4502				
2000mg/l							
A	3.4970	0.1303	0.3667	0.3325	0.16714	0.2210	89.79
B	4.4598	4.1615	0.2983				
2500mg/L							
A	3.3717	3.1008	0.2709	0.2915	0.16714	0.1938	90.84
B	3.5895	3.2641	0.3254				

Table 4. 25: Weight loss(g), corrosion rate(g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion In 1 M HCL with andwithout water extract of LH after 288 hours

System	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight Loss(g)	Area of Coupon Cm^2	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.1842	1.5545	1.6297	1.7814	0.16714	0.8882	------
B	3.5540	1.6209	1.9331				
500mg/L							
A	3.4081	3.0981	0.3100	0.31485	0.16714	0.1570	82.33
B	3.5854	3.2657	0.3197				
1000mg/L							
A	3.4275	3.2684	0.1591	0.15205	0.16714	0.0758	91.46
B	3.2763	3.1313	0.1450				
1000mg/l							
A	3.3034	3.1698	0.1336	0.1367	0.16714	0.0682	92.32
B	3.5730	3.3519	0.1398				
2000mg/L							
A	3.4095	3.2798	0.1297	0.11365	0.16714	0.0567	93.62
B	3.4467	3.3491	0.0976				
2500mg/l							
A	3.2689	3.1667	0.1022	0.10135	0.16714	0.0505	94.31
B	3.3384	3.2379	0.1005				

Table 4.26: Weight loss(g), corrosion rate(g/cm^{2}hr) and inhibition efficiency(%) values of mild steel corrosion in 1M H_2SO_4 with andwithout water extract of OG after 288 hours.

System	Initial Weight (g)	Final Weight (g)	Weight Loss(g)	Average Weight Loss(g)	Area of Coupon Cm^2	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.4014	1.1067	2.2947	2.27255	0.16714	1.1331	------
B	3.3923	1.1419	2.2504				
500mg/L							
A	3.3696	3.1722	0.1974	0.18135	0.16714	0.0904	92.02
B	3.3795	3.2142	0.1653				
1000mg/L							
A	3.5119	3.3439	0.1680	0.16105	0.16714	0.0803	92.91
B	3.3604	3.2063	0.1541				
1500mg/L							
A	3.6410	3.4848	0.1562	0.1571	0.16714	0.0783	93.09
B	3.7663	3.6083	0.1580				
2000mg/l							
A	3.0119	2.8796	0.1323	0.133	0.16714	0.0663	94.14
B	3.7604	3.6267	0.1337				
2500mg/l							
A	3.5415	3.4097	0.1318	0.11885	0.16714	0.0593	94.77
B	3.4667	3.3608	0.1059				

Table 4.27: Weight loss(g), corrosion rate(g/cm^{2}hr) and inhibition efficiency(%) values of mild steel in 0.5 M H_2SO_4 with and without water extract of LH after 288 hours

System	Initial Weight(g)	Final Weight(g)	Weight Loss(g)	Average Weight Loss(g)	Area of Coupon Cm^2	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank							
A	3.4878	0.0000	3.4878	3.37085	0.16714	1.6807	------
B	3.2539	0.0000	3.2539				
500mg/L							
A	3.2575	2.0013	1.2562	1.3003	0.16714	0.6483	61.43
B	3.3894	2.0450	1.3444				
1000mg/L							
A	3.5197	2.4006	1.1191	1.1080	0.16714	0.5524	67.13
B	3.4407	2.3437	1.0970				
1500mg/L							
A	3.3612	2.5797	0.7815	0.7995	0.16714	0.3986	76.28
B	3.4114	2.5939	0.8175				
2000mg/l							
A							
B	3.4960	2.8043	0.6917	0.6379	0.16714	0.3180	81.07
	3.3613	2.7772	0.5841				
2500mg/l							
A	3.4844	3.1819	0.3025	0.5831	0.16714	0.2907	82.70
B	3.3378	3.0572	0.2806				

Table 4.28 : Weight loss(g), corrosion rate (g/cm^{2}hr) and inhibition efficiency(%) values of mild steel in 1M HCl with and without aqueous extract of OG after 288 hours

System	Initial weight(g)	Final weight(g)	Weightt loss(g)	Average weight loss (g)	Area of coupon in cm^2	Corrosion rate (g/cm^{2}hr)	Inhibition efficiency (%)
Blank							
A	3.4000	3.4000	3.4000	3.40965	0.16714	1.700	-------
B	3.4193	3.4193	3.4193				
500mg/l							
A	3.3787	2.5761	0.8026	0.7637	0.16714	0.3808	77.60
B	3.2273	2.5025	0.7248				
1000mg/l							
A	3.6276	3.0382	0.5894	0.6153	0.16714	0.3068	81.95
B	3.5786	2.9375	0.6411				
1500mg/l							
A	3.5039	2.9298	0.5761	0.5847	0.16714	0.2915	82.85
B	3.2967	2.7034	0.5933				
2000mg/l							
A	3.4484	3.0593	0.3891	0.4093	0.16714	0.2040	87.99
B	3.2512	2.8217	0.4295				
2500mg/l							
A	3.5059	3.4109	0.0950	0.09285	0.16714	0.0463	97.27
B	3.2967	2.2060	0.0907				

4.2 ANALYSIS OF RESULTS FROM GRAVIMERTIC MEASUREMENT

Results obtained from weight loss measurement on the inhibition effect of *Landolphia heudelotii (LH)* and *Ocimum gratissimum(OG)* on mild steel corrosion in 1 M HCl and 0.5 M H_2SO_4 is shown in tables **4.1 – 4.28** above. Results obtained revealed the following:

4.2.1 VARIATION OF AVERAGE WEIGHT LOSS WITH VARIOUS CONCENTRATIONS OF LH AND OG IN 1 M HCl AND 0.5 M H_2SO_4

From the tables of results in **4.1 - 4.28** above and figures **4.1 – 4.7** below it shows that the average weight loss decreased with increase in concentration of aqueous extract of LH and OG in both test media. Highest weight loss was recorded in the absence of both plant extracts than in their presence This can be attributed to the fact that at high concentration more of the phyto-constituent are available for adsorption at the metal/solution interphase, hence formation of the protective film becomes more enhanced, this reduces attack on the mild steel hence the decrease in weight loss.

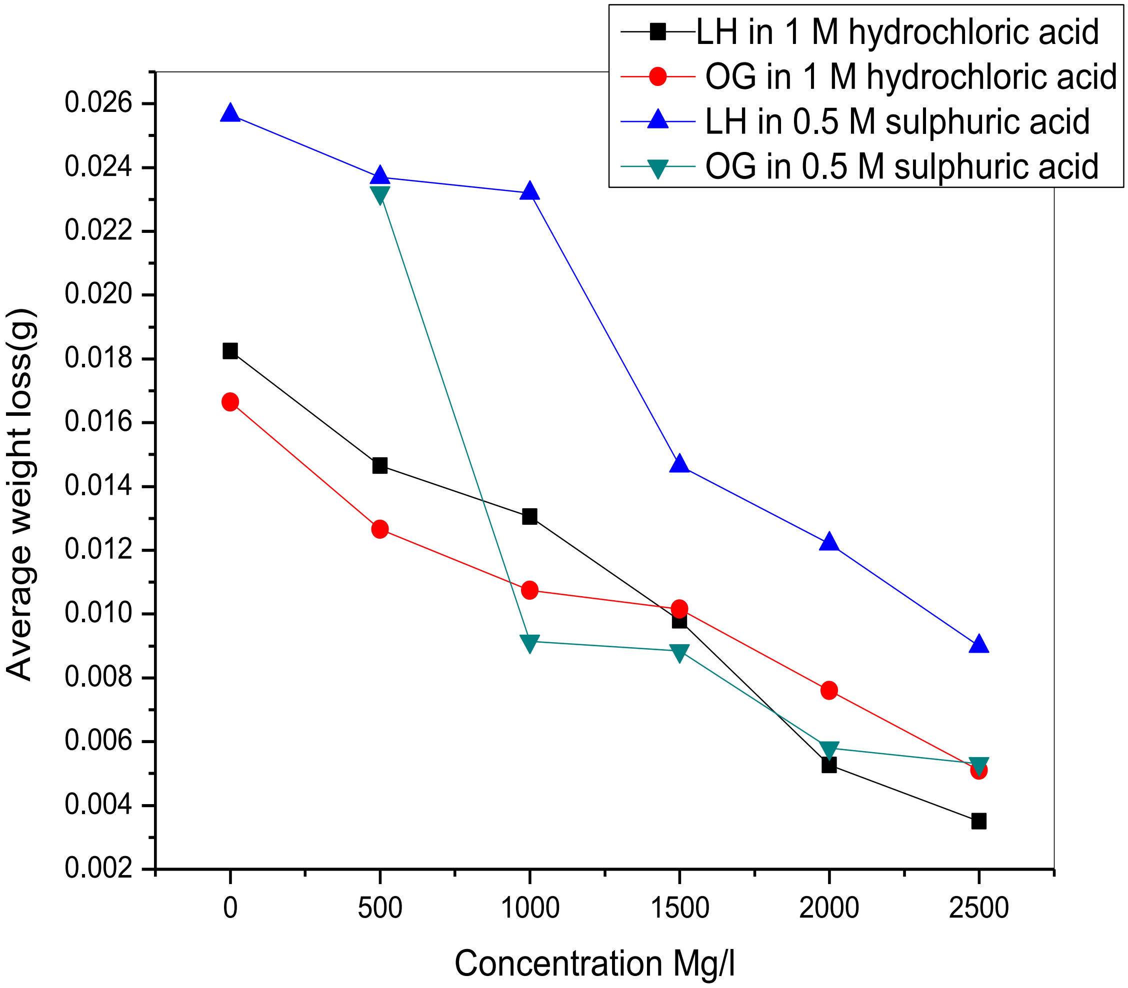

Figure 4.1 : Variation of weight loss with various concentration of LH and OG in 1 M HCl and 0.5 M H_2SO_4 after three hour

Weight loss decreased with increase in concentration of the aqueous extracts of LH and OG in both test media, highest weight loss was recorded in the absence of the plant extracts while as the concentration of the plant extracts were increased, weight loss decreased.

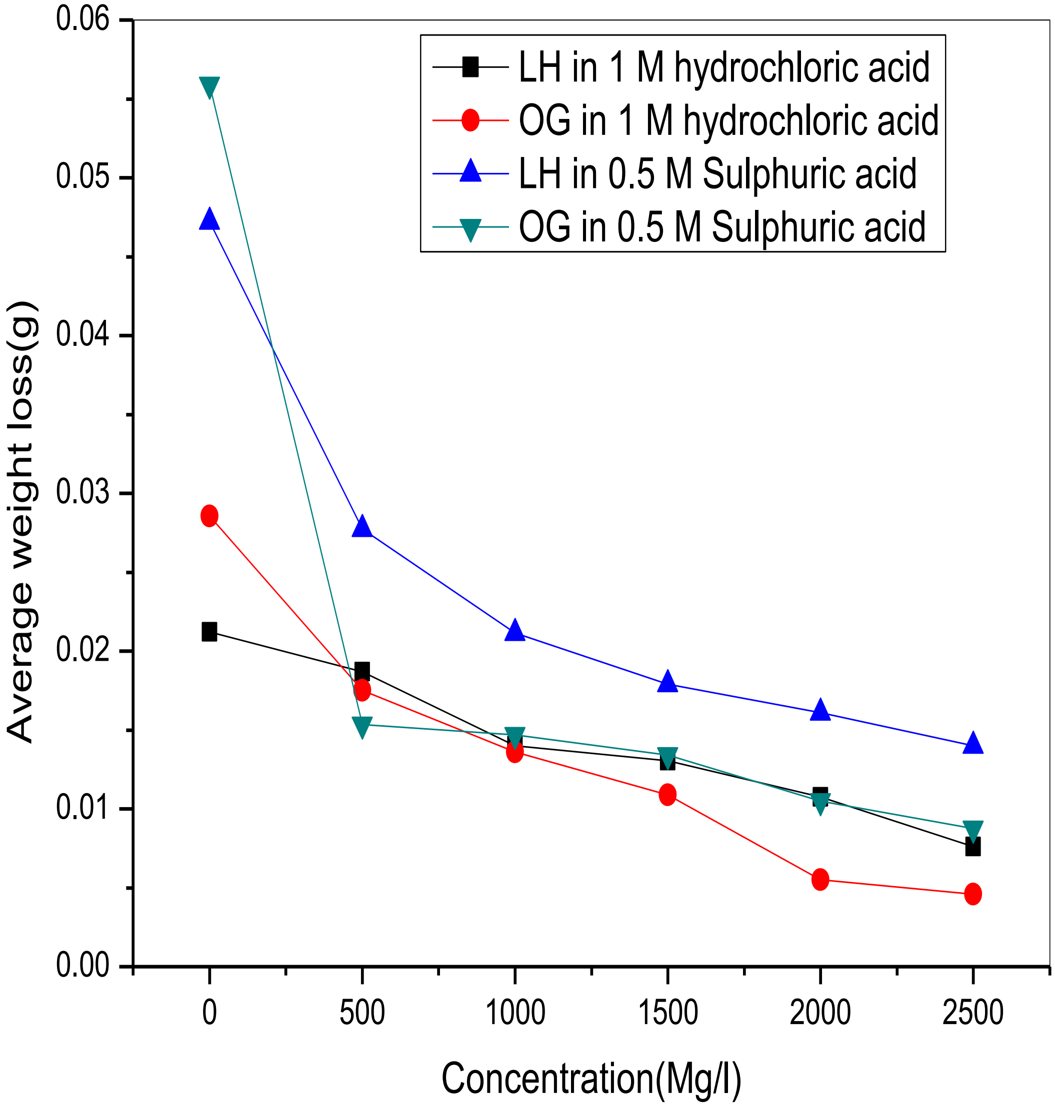

Figure 4.2: Variation of weight loss with various concentrations of LH and OG in 1M HCl and 0.5 M H_2SO_4 after six hours.

Weight loss decreased with increase in concentration of the aqueous extracts of LH and OG in both test media, highest weight loss was recorded in the absence of the plant extracts while as the concentration of the plant extracts were increased, weight loss decreased

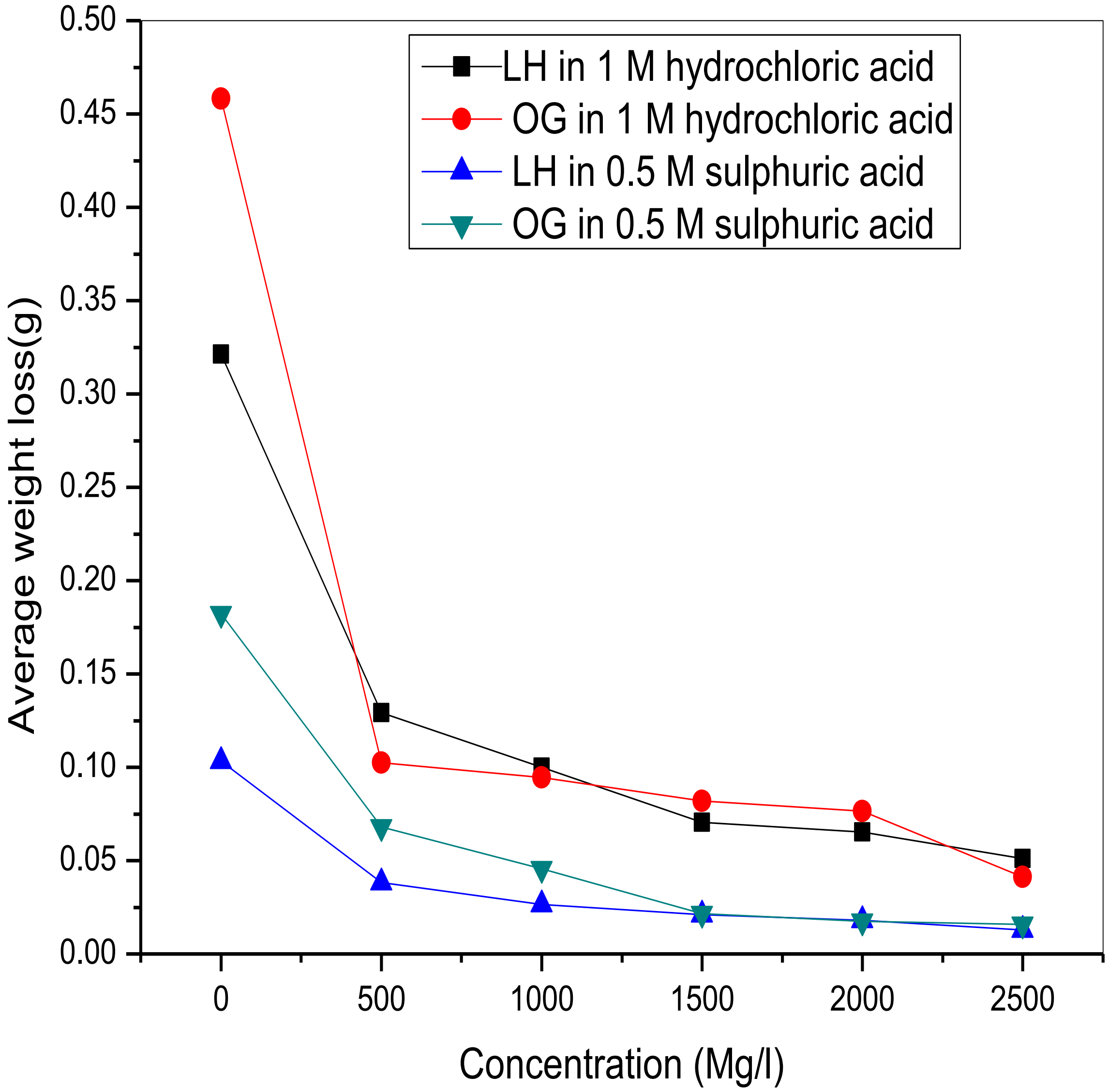

Figure 4.3 : Variation of weight loss with various concentration of LH and OG in 1 M HCl and 0.5 M H_2SO_4 after 24 hours

Weight loss decreased with increase in concentration of the aqueous extracts of LH and OG in both test media, highest weight loss was recorded in the absence of the plant extracts while as the concentration of the plant extracts were increased, weight loss decreased

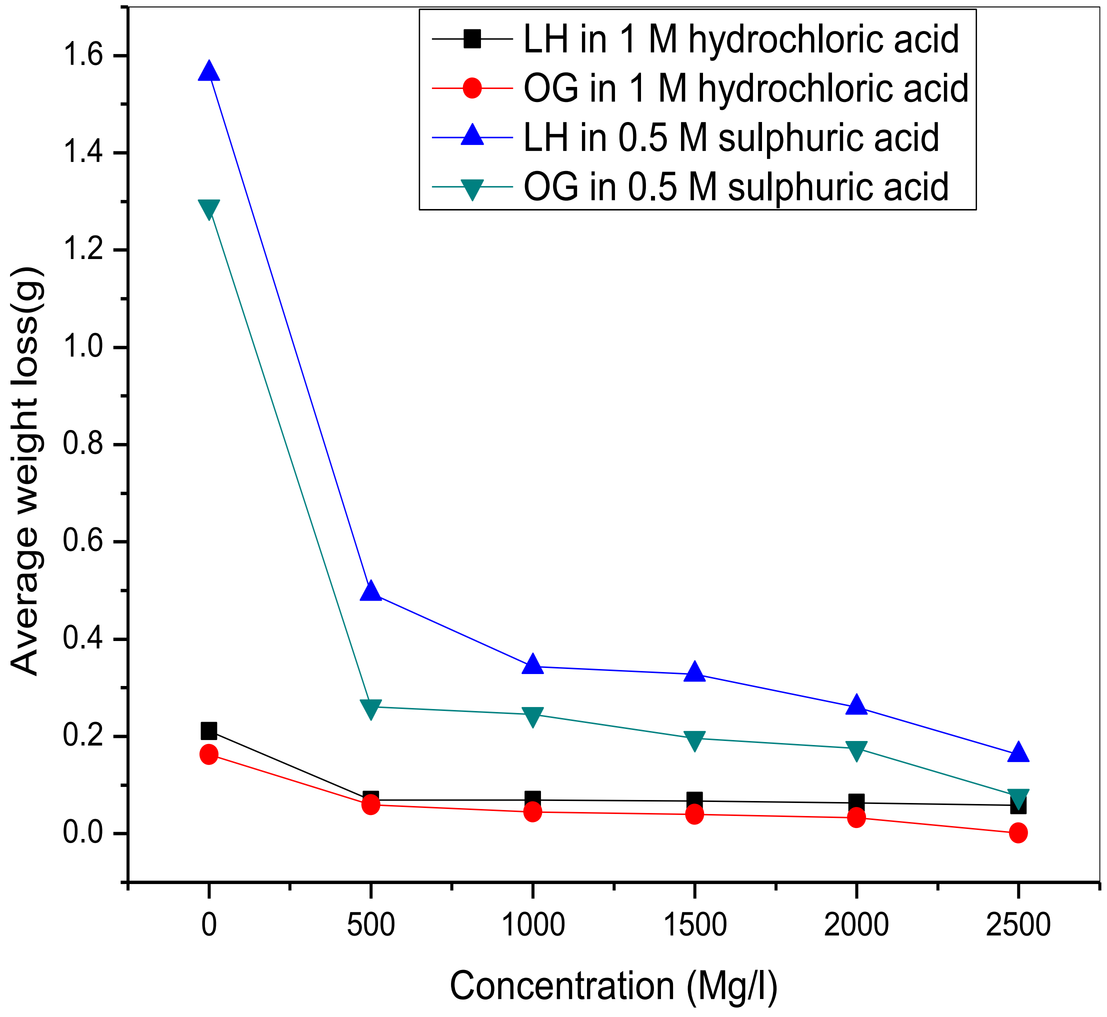

Figure 4.4 : Variation of weight loss with various concentration of LH and OG in 1 M HCl and 0.5 M H_2SO_4 after 72 hours

Weight loss decreased with increase in concentration of the aqueous extracts of LH and OG in both test media, highest weight loss was recorded in the absence of the plant extracts while as the concentration of the plant extracts were increased, weight loss decreased.

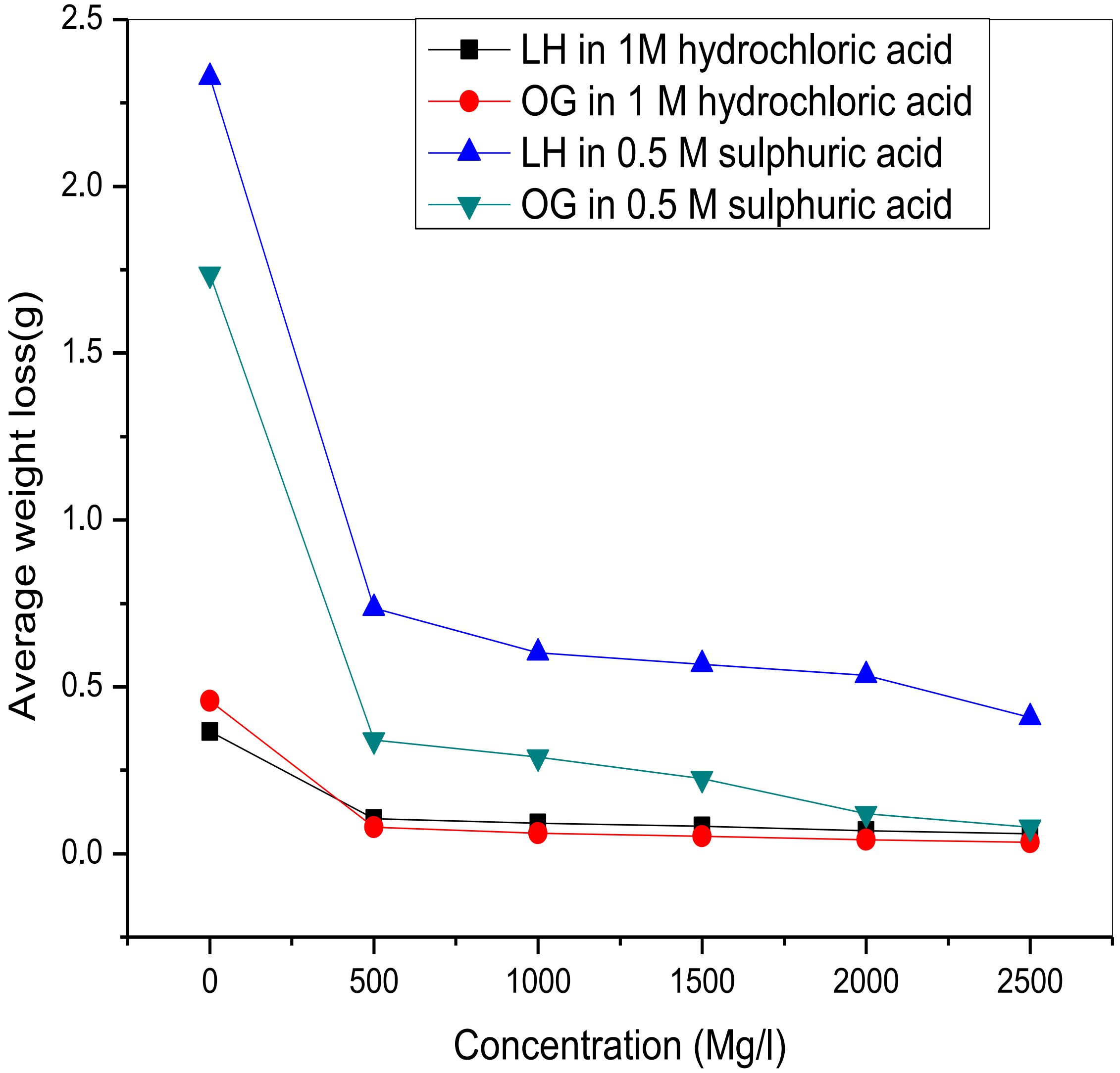

Figure 4. 5 : Variation of weight loss with various concentration of LH and OG in 1 M HCl and 0.5 M H_2SO_4 after 144 hours

Weight loss decreased with increase in concentration of the aqueous extracts of LH and OG in both test media, highest weight loss was recorded in the absence of the plant extracts while as the concentration of the plant extracts were increased, weight loss decreased

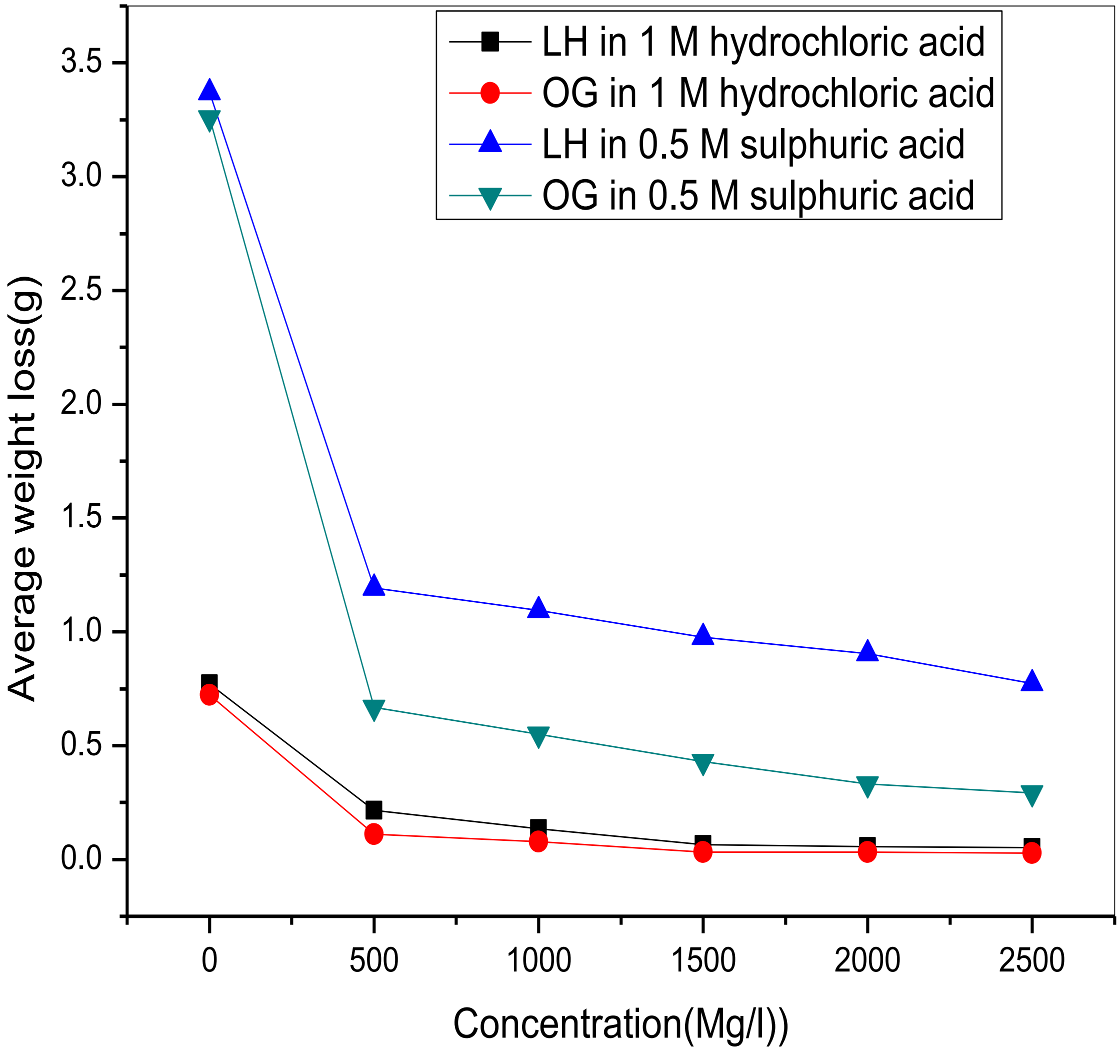

Figure 4. 6 : Variation of weight loss with various concentrations of LH and OG in 1 M HCl and 0.5 M H_2SO_4 after 216 hours

Weight loss decreased with increase in concentration of the aqueous extracts of LH and OG in both test media, highest weight loss was recorded in the absence of the plant extracts while as the concentration of the plant extracts were increased, weight loss decreased.

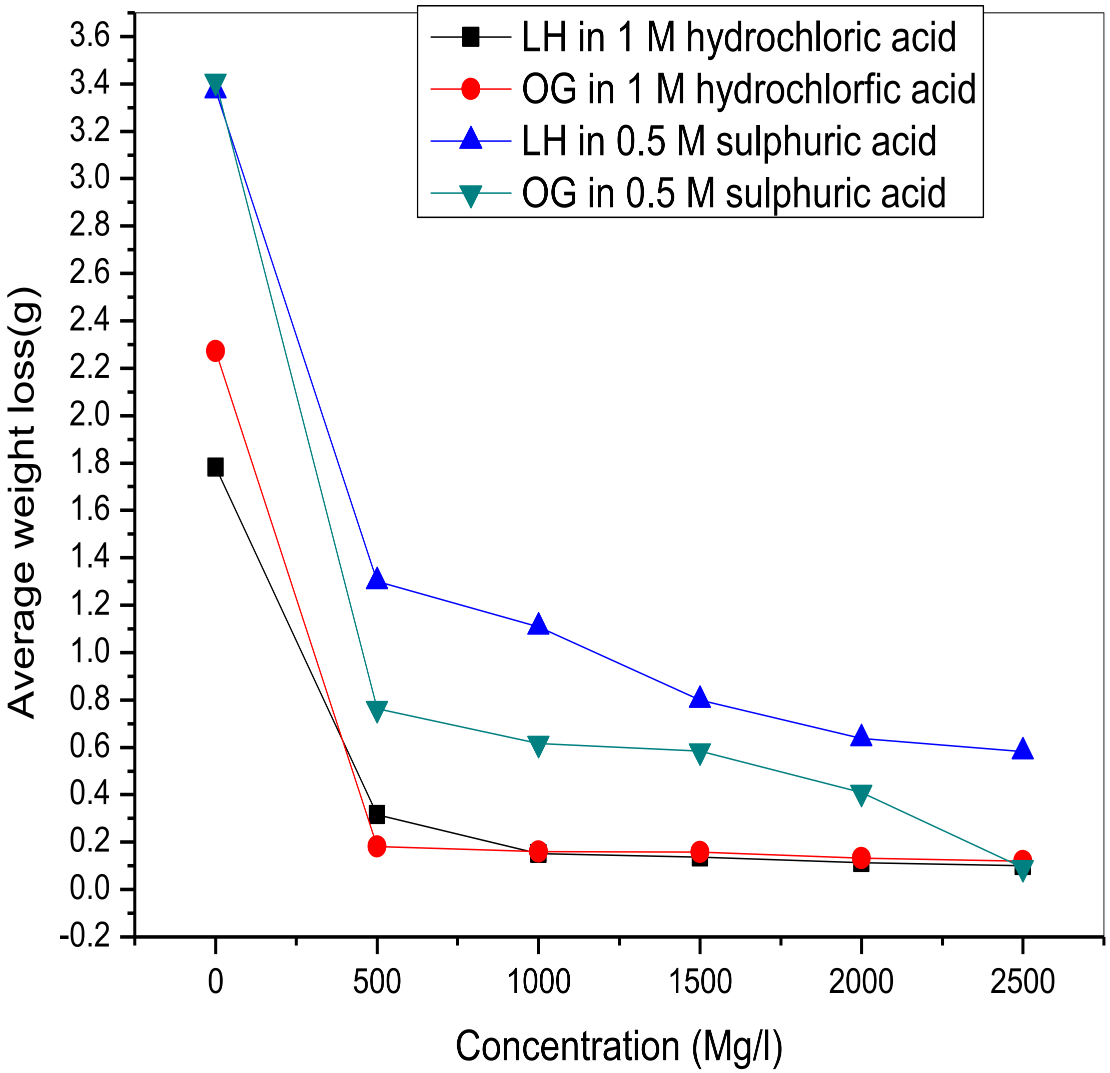

Figure 4. 7 : Variation of weight loss with various concentrations of LH and OG in 1 M HCl and 0.5 M H_2SO_4 after 288 hours.

Weight loss decreased with increase in concentration of the aqueous extracts of LH and OG in both test media, highest weight loss was recorded in the absence of the plant extracts while as the concentration of the plant extracts were increased, weight loss decreased.

4.2.2 VARIATION OF CORROSION RATE WITH VARIOUS CONCENTRATIONS OF LH AND OG IN 1 M HCl AND 0.5 M H_2SO_4 AT VARIOUS IMMERSION TIME.

Experimental results shown in tables **4.1 – 4.28** above and figures **4.8 – 4.13** below reveals a decrease in corrosion rate with increase in concentration of LH and OG in both test media, highest corrosion rate was recorded in the absence of both plant extracts than in their presence. The effect is due to the fact that at high concentration more of the phytoconsistuent are available for adsorption and formation of the protective film of insoluble organic complex on the mild steel surface is enhanced, hence corrosion rate decreases. In addition, lower corrosion rate was observed in HCl than H_2SO_4, the result can be attributed to the nature of acid anion and type of inhibitor, according to literature halide ions are more readily adsorbed thus, Cl^- ions are easily adsorbed than SO_4^{2-} ions and protonated inhibitors are less adsorbed on a corroding metal species which is positively charged hence the ability of Cl^- ions to be more readily adsorbed facilitates the adsorption of the phytoconsistuent presence in both plant extract for the formation of the film of insoluble organic compound that protects the metal specimen resulting to higher corrosion rate in H_2SO_4 than HCl .

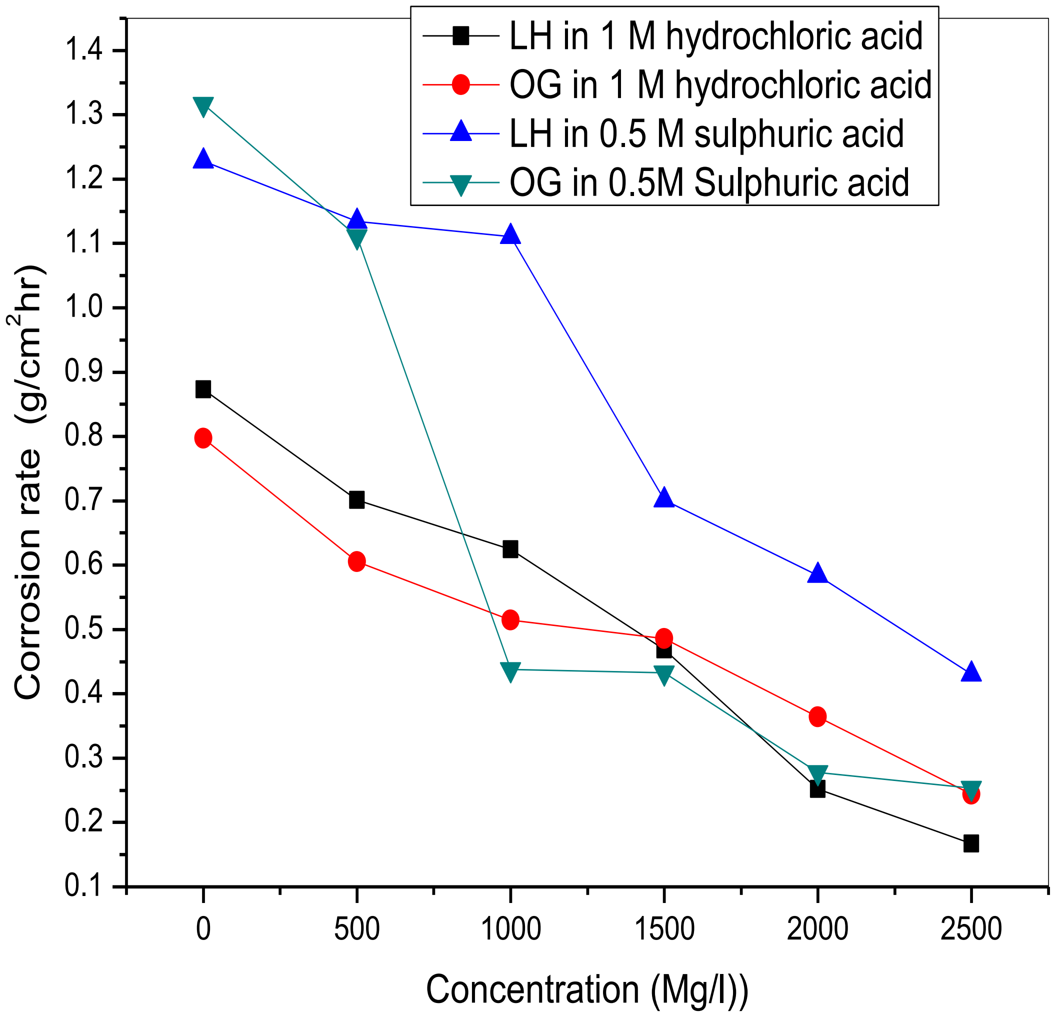

Figure 4. 8 : Variation of corrosion rate with various Concentration of LH and OG in 1 M HCl and 0.5 M H_2SO_4 after three hours

Corrosion rate decreased with increase in concentration of the aqueous extracts of LH and OG in both test media, highest corrosion rate was recorded in the absence of the plant extracts while as the concentration was increased the corrosion rate decreased.

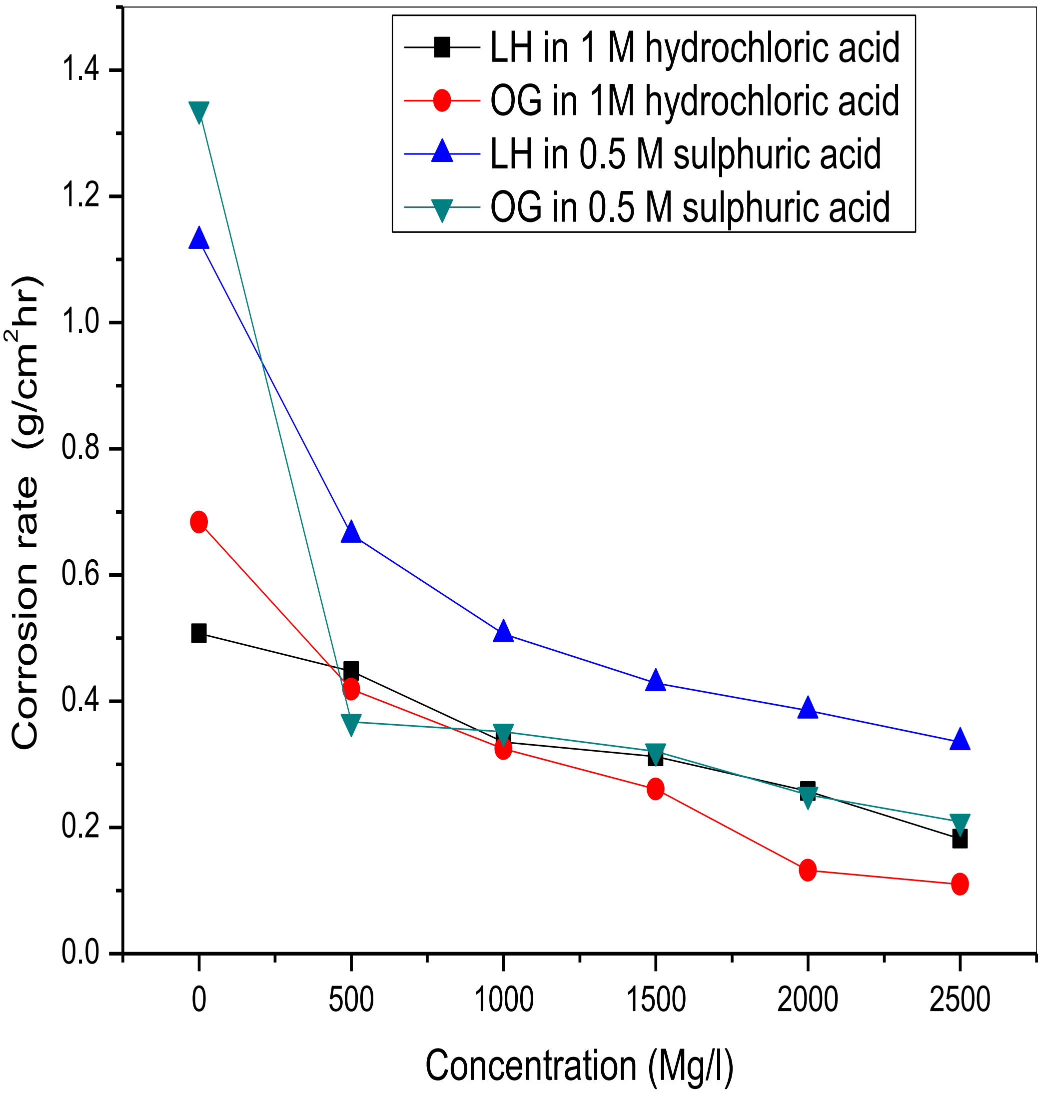

Figure 4.9: Variation of corrosion rate with various concentration of LH and OG in 1 M HCl and 0.5 M H_2SO_4 after six hours.

Corrosion rate decreased with increase in concentration of the aqueous extracts of LH and OG in both test media, highest corrosion rate was recorded in the absence of the plant extracts while as the concentration was increased the corrosion rate decreased.

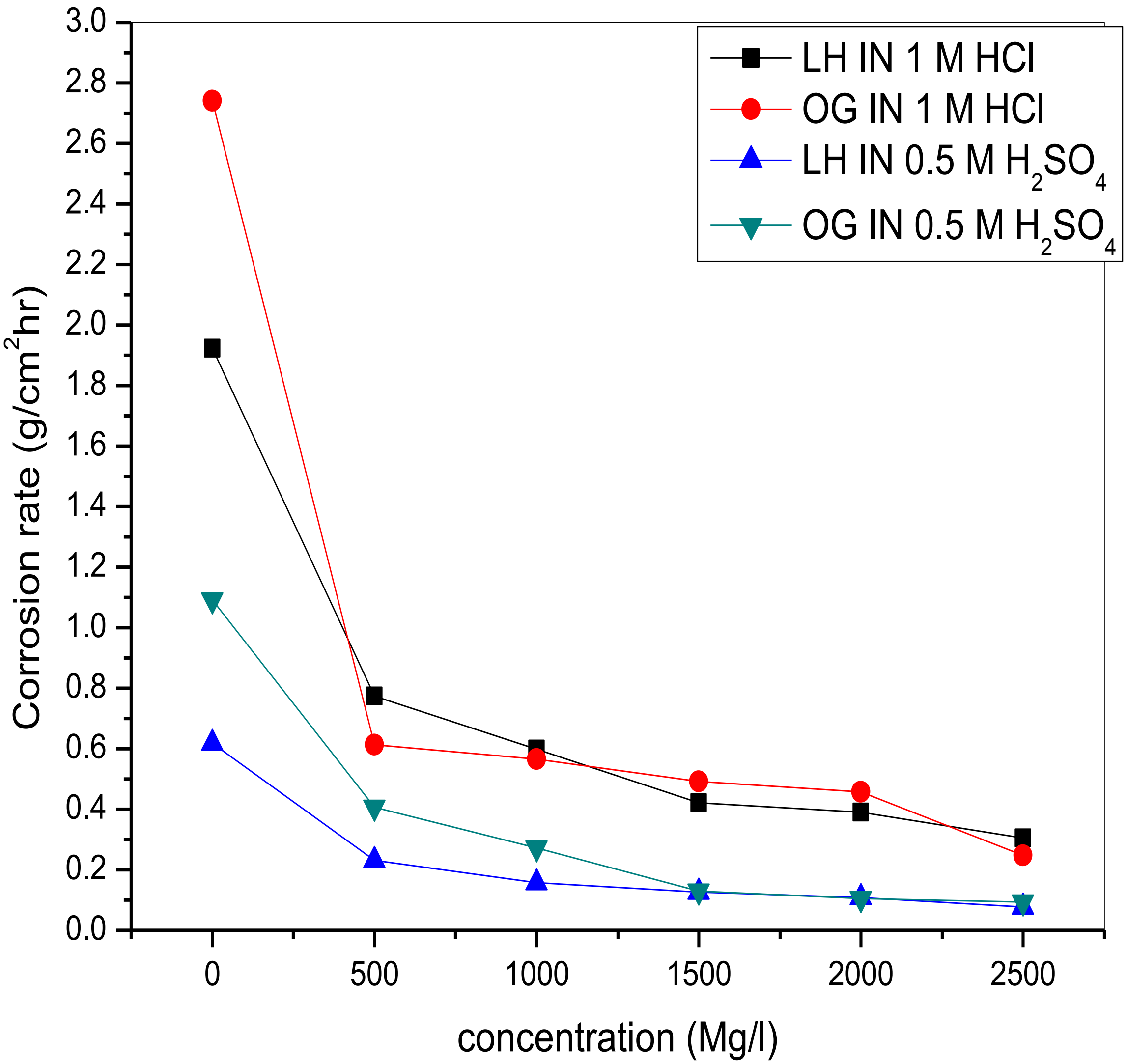

Figure 4. 10: Variation of Corrosion rate with various concentrations of LH and OG in 1 M HCl and 0.5 M H_2SO_4 after 24 hours

Corrosion rate decreased with increase in concentration of the aqueous extracts of LH and OG in both test media , highest corrosion rate was recorded in the absence of the plant extracts while as the concentration was increased the corrosion rate decreased.

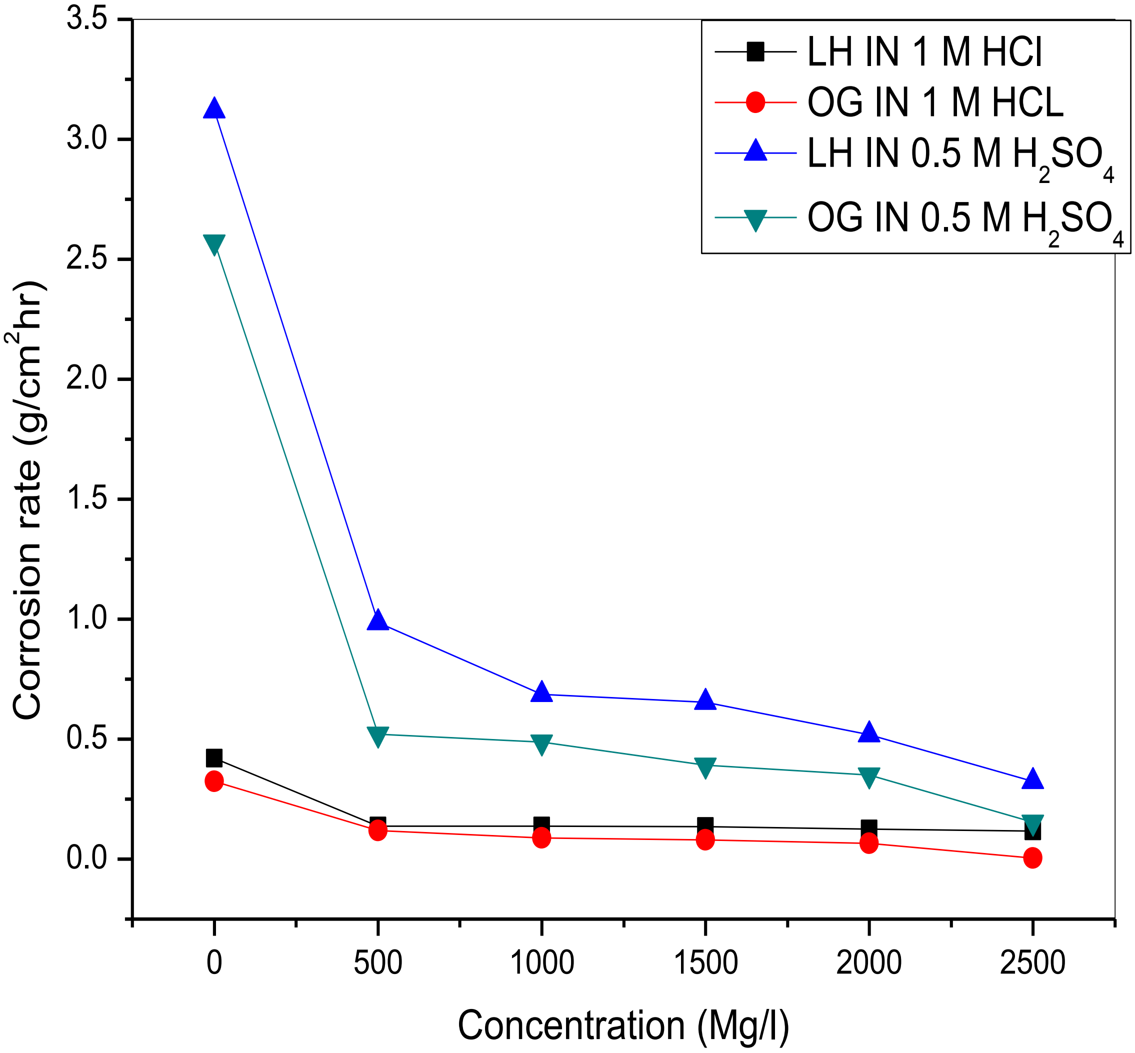

Figure 4.11 : Variation of corrosion rate with various concentrations of LH and OG after in 1M HCl and 0.5 M H_2SO_4 72 hours.

Corrosion rate decreased with increase in concentration of the aqueous extracts of LH and OG in both test media , highest corrosion rate was recorded in the absence of the plant extracts while as the concentration was increased the corrosion rate decreased.

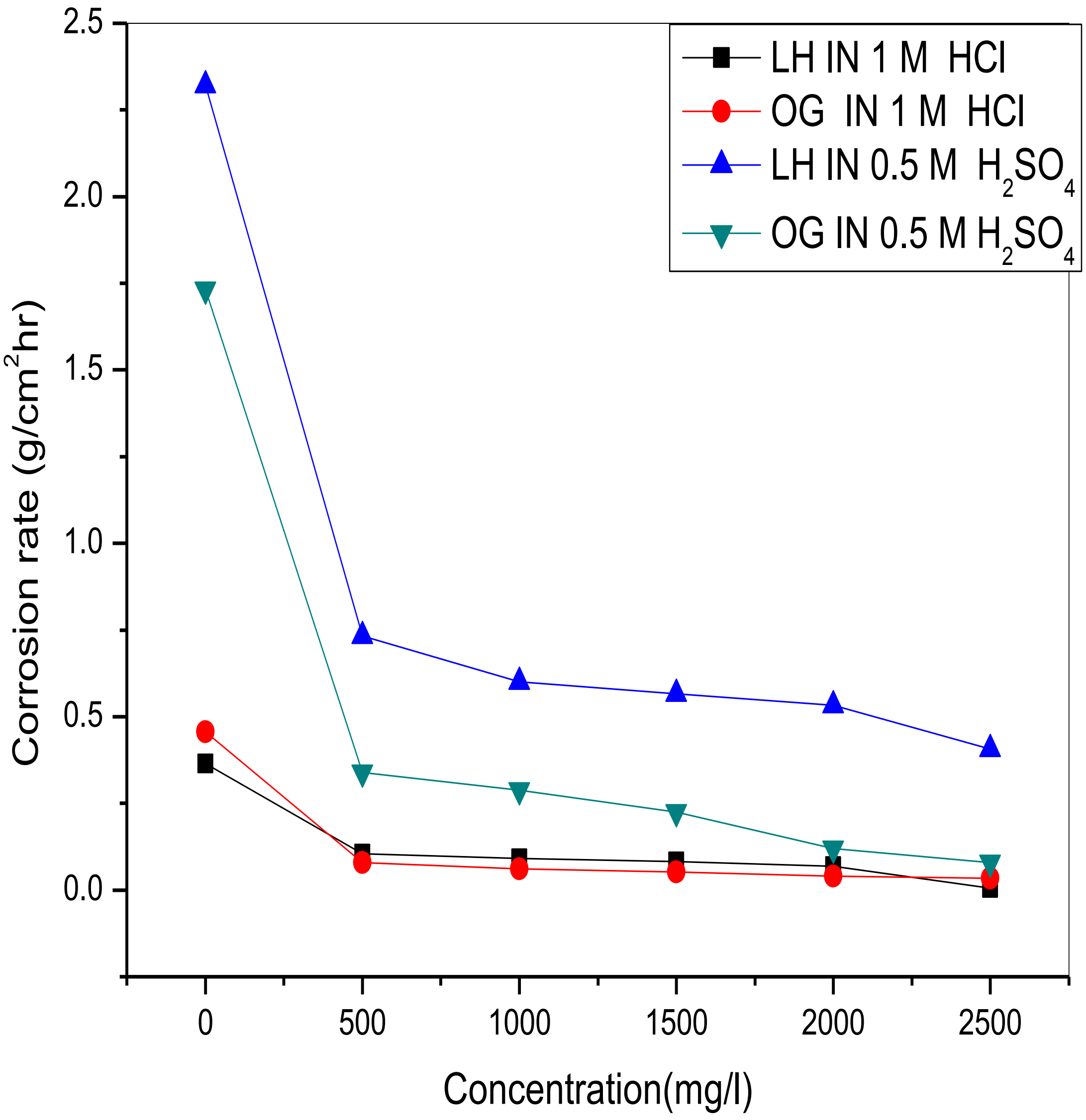

Figure 4.12: Variation of Corrosion rate with various concentration of LH and OG in 1 M HCl and 0.5 M H_2SO_4 after 144 hours

Corrosion rate decreased with increase in concentration of the aqueous extracts of LH and OG in both test media , highest corrosion rate was recorded in the absence of the plant extracts while as the concentration was increased the corrosion rate decreased.

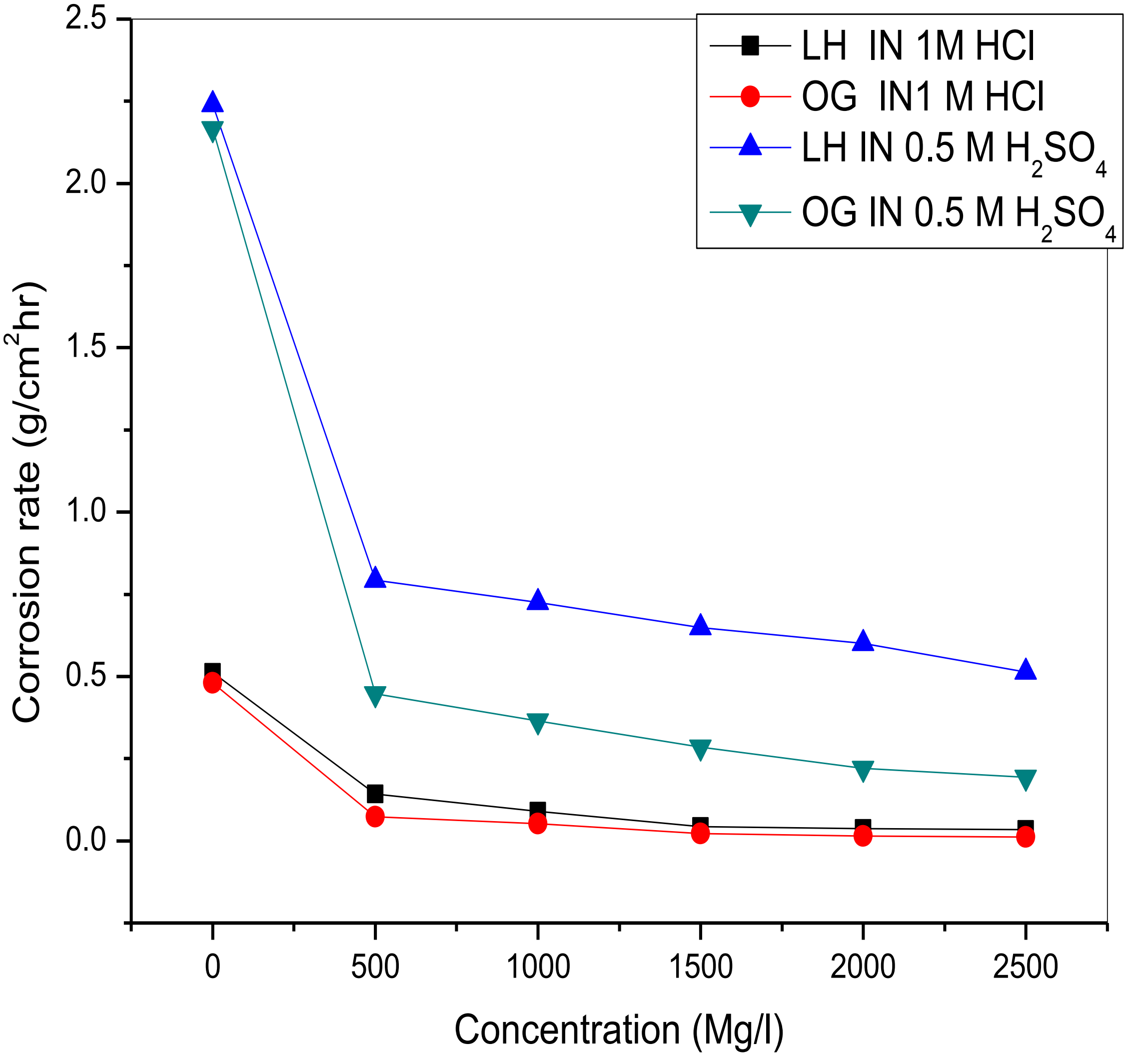

Figure 4.13 : Variation of corrosion rate with various concentrations of LH and OG in 1 M HCl and 0.5 M H_2SO_4 after 216 hours

Corrosion rate decreased with increase in concentration of the aqueous extracts of LH and OG in both test media , highest corrosion rate was recorded in the absence of the plant extracts while as the concentration was increased the corrosion rate decreased.

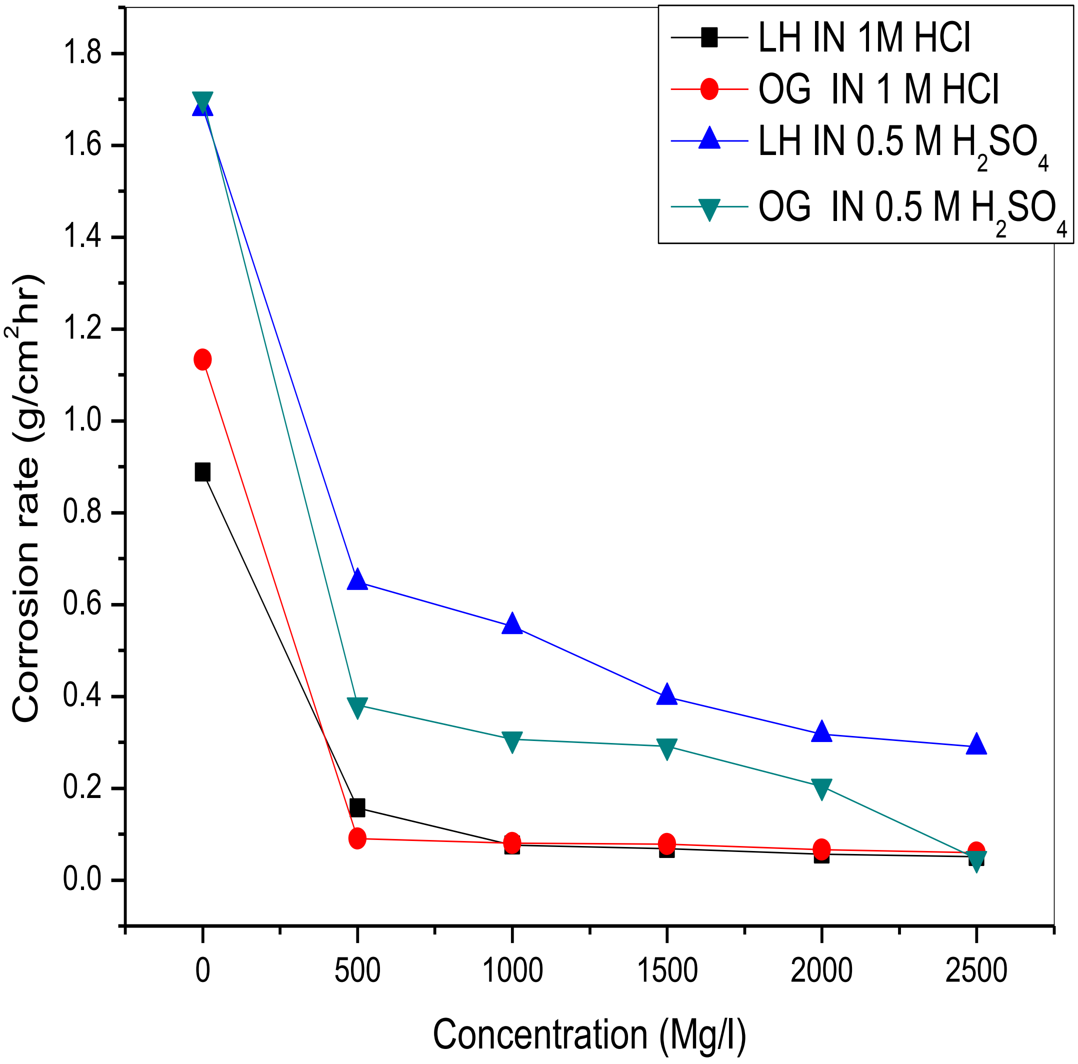

Figure 4.14 : Variation of corrosion rate with various concentrations of LH and OG in 1M HCl and 0.5 M H_2SO_4 after 288 hours

Corrosion rate decreased with increase in concentration of the aqueous extracts of LH and OG in both test media , highest corrosion rate was recorded in the absence of the plant extracts while as the concentration was increased the corrosion rate decreased.

4.2.3. VARIATION OF INHIBITION EFFICIENCY WITH VARIOUS CONCENTRATION OF OG AND LH IN 1 M HCl AND 0.5 M H_2SO_4.

Results obtained as shown in tables **4.1. – 4.28** above and figures **4.14 - 4.20** below reveals an increase in inhibition efficiency with increase in concentration and immersion time of LH and OG in both test media. Highest inhibition efficiency of 97.27% and 94.31% was recorded in OG and LH at 2500mg/l in 1M HCl after twelve days respectively. The effect indicates strong adsorption of the phytoconsistuent present in OG and LH on the surface of the mild steel at higher concentration at the metal solution interphase, surface coverage increases and the metal surface is more protected from corrosion. The result is consistent with the works of (Oguzie *et al.*, 2010; Raja *et al.*, 2009).

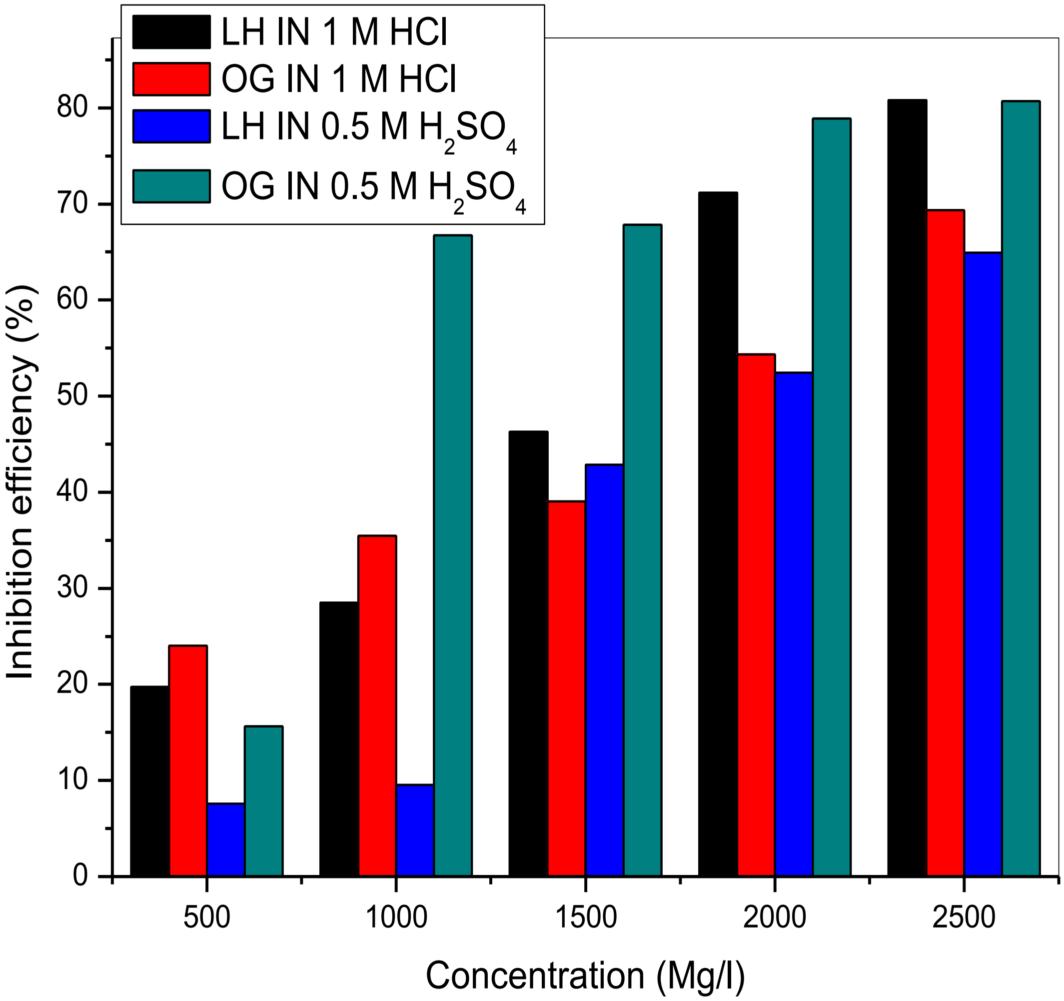

Figure 4.15 : Variation of inhibition efficiency with various concentration of LH and OG in 1 M HCl and 0.5 M H_2SO_4 after three hours

Inhibition efficiency increased with increase in concentration of the aqueous extracts of LH and OG in both teat media.

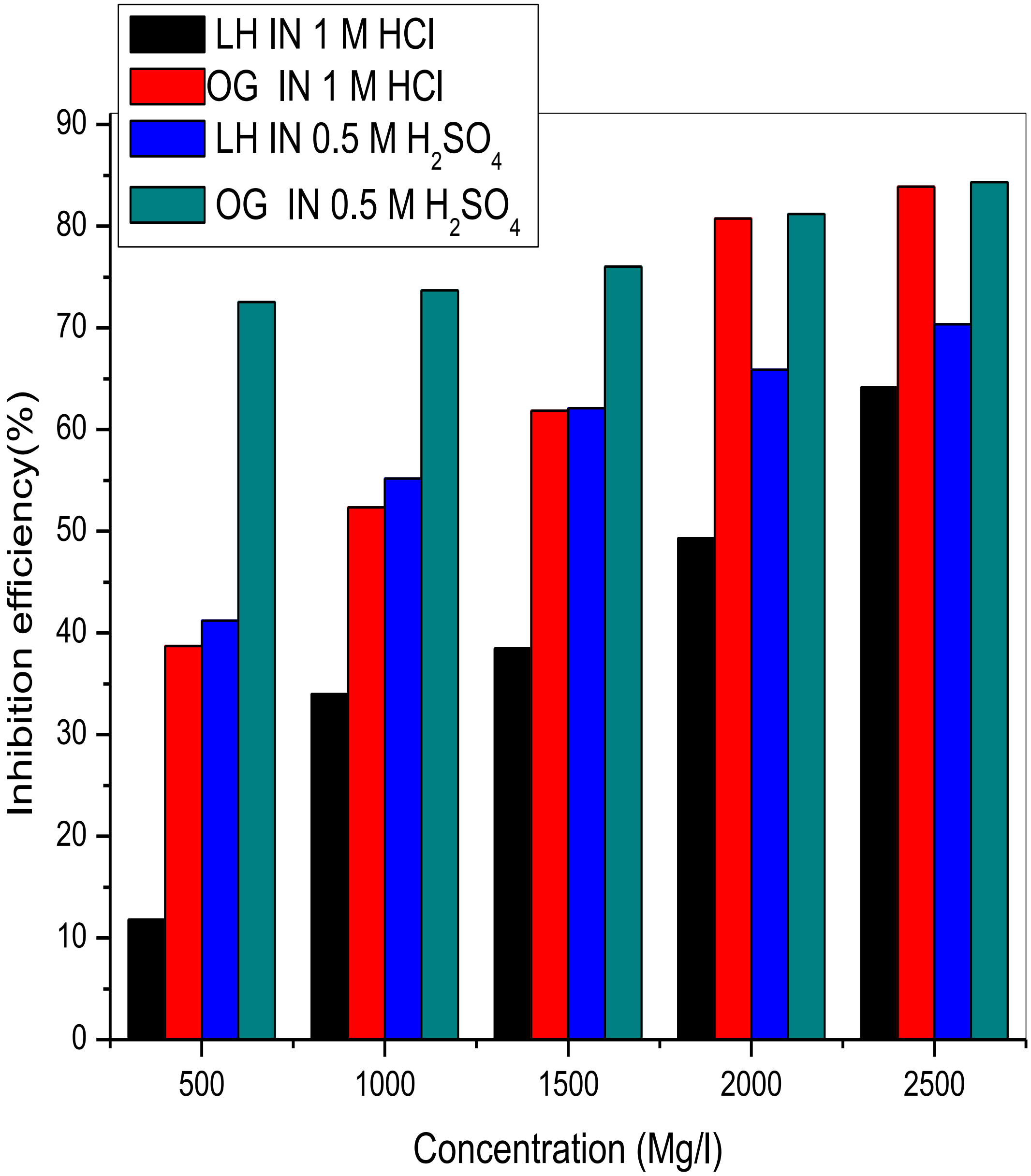

Figure 4.16 : Variation of inhibition efficiency with various concentration of LH and OG in 1 M HCl and 0.5 M H_2SO_4 after six hours.

Inhibition efficiency increased with increase in concentration of the aqueous extracts of LH and OG in both teat media.

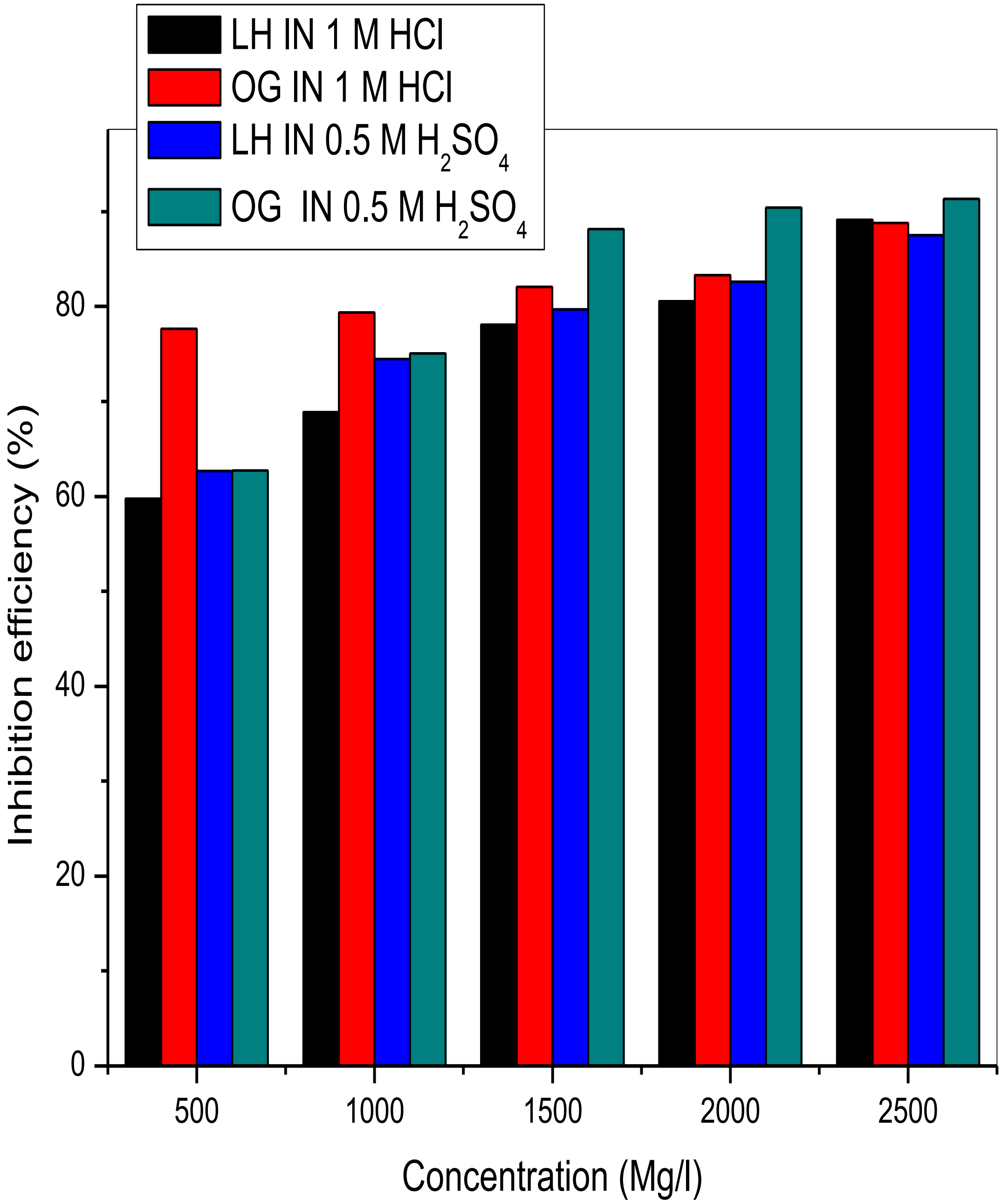

Figure 4.17 : Variation of Inhibition efficiency with various concentration of LH and OG in 1M HCl and 0.5 M H_2SO_4 after 24 hours

Inhibition efficiency increased with increase in concentration of the aqueous extracts of LH and OG in both teat media.

.

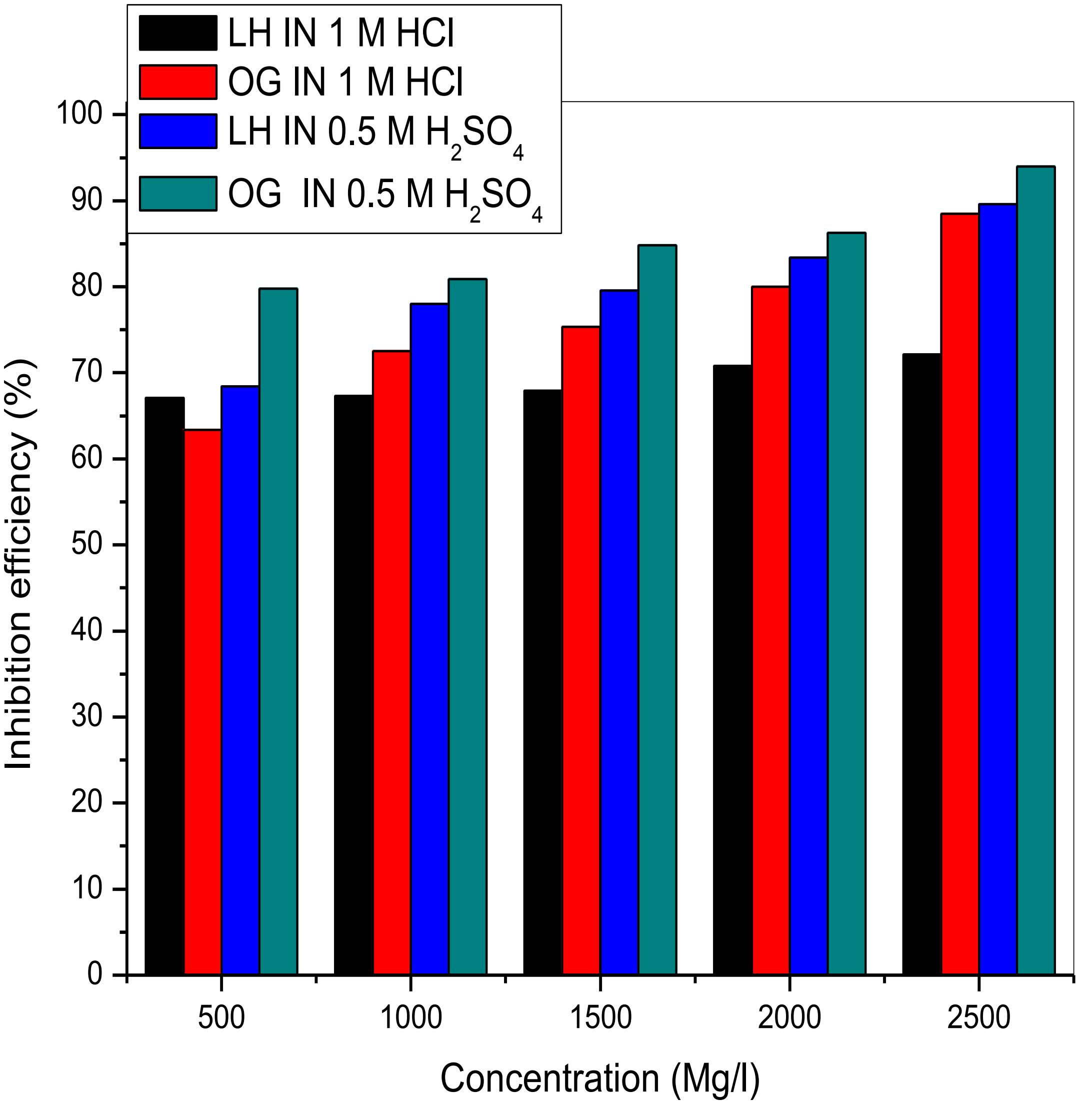

Figure 4.18 : Variation of Inhibition efficiency with various concentrations of LH and OG in 1M HCl and 0.5 M H_2SO_4 after three days.

Inhibition efficiency increased with increase in concentration of the aqueous extracts of LH and OG in both teat media.

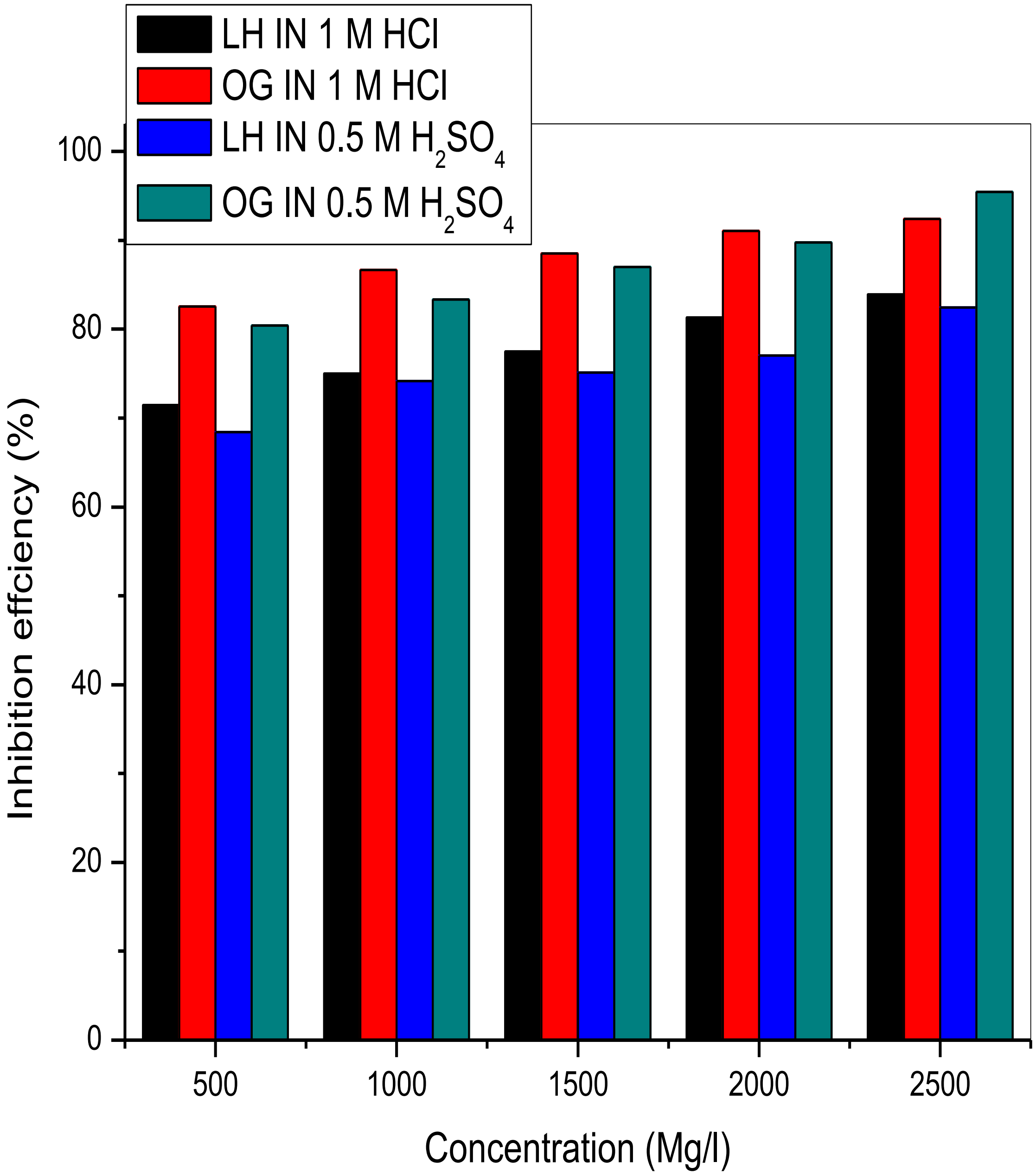

Figure 4.19 : Variation of Inhibition efficiency with various concentrations of LH and OG in 1M HCl and 0.5 M H_2SO_4 after six days.

Inhibition efficiency increased with increase in concentration of the aqueous extracts of LH and OG in both teat media.

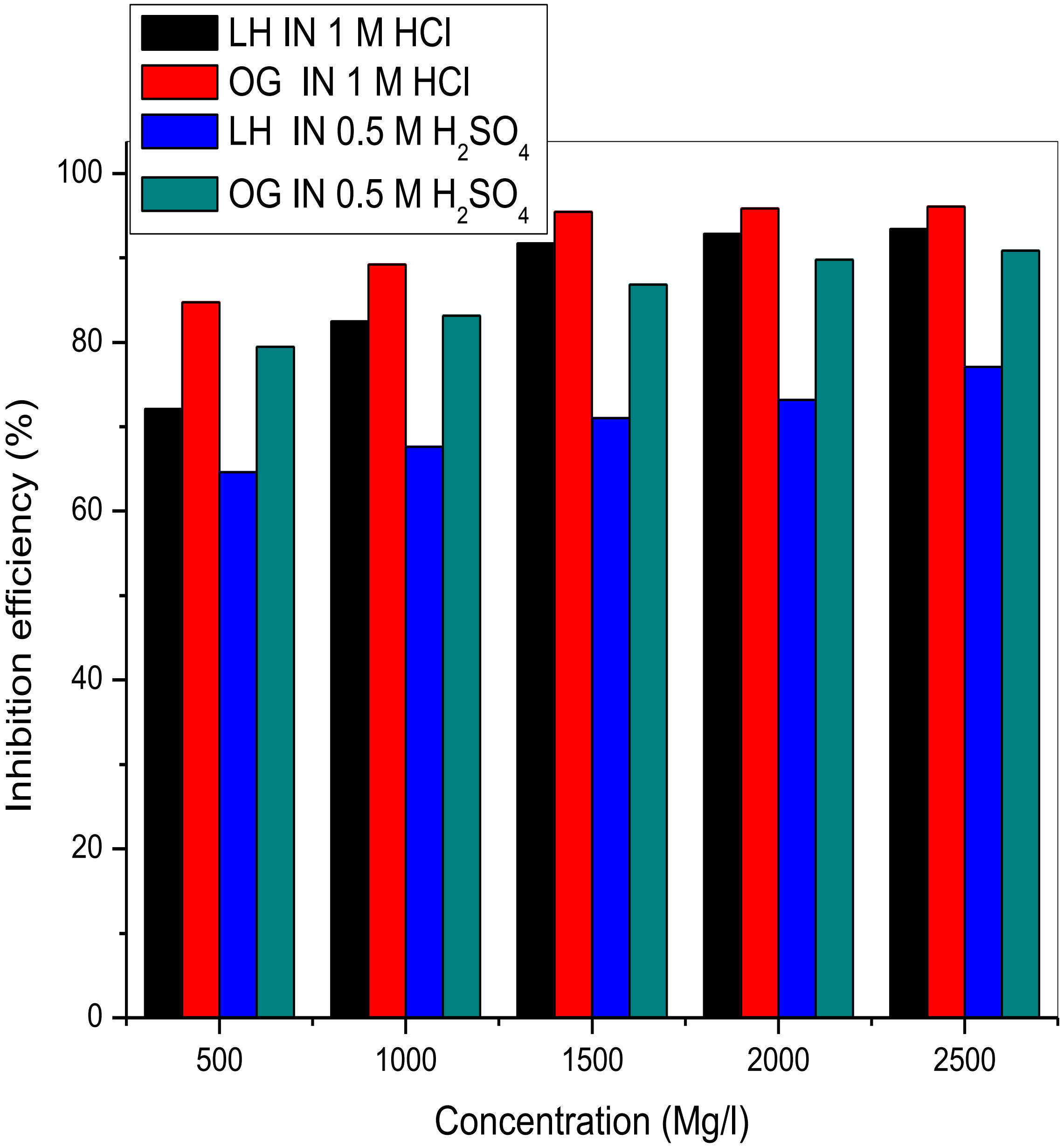

Figure 4.20 : Variation of Inhibition efficiency with various concentrations of LH and OG in 1 M HCl and 0.5 M H_2SO_4 after nine days.

Inhibition efficiency increased with increase in concentration of the aqueous extracts of LH and OG in both teat media.

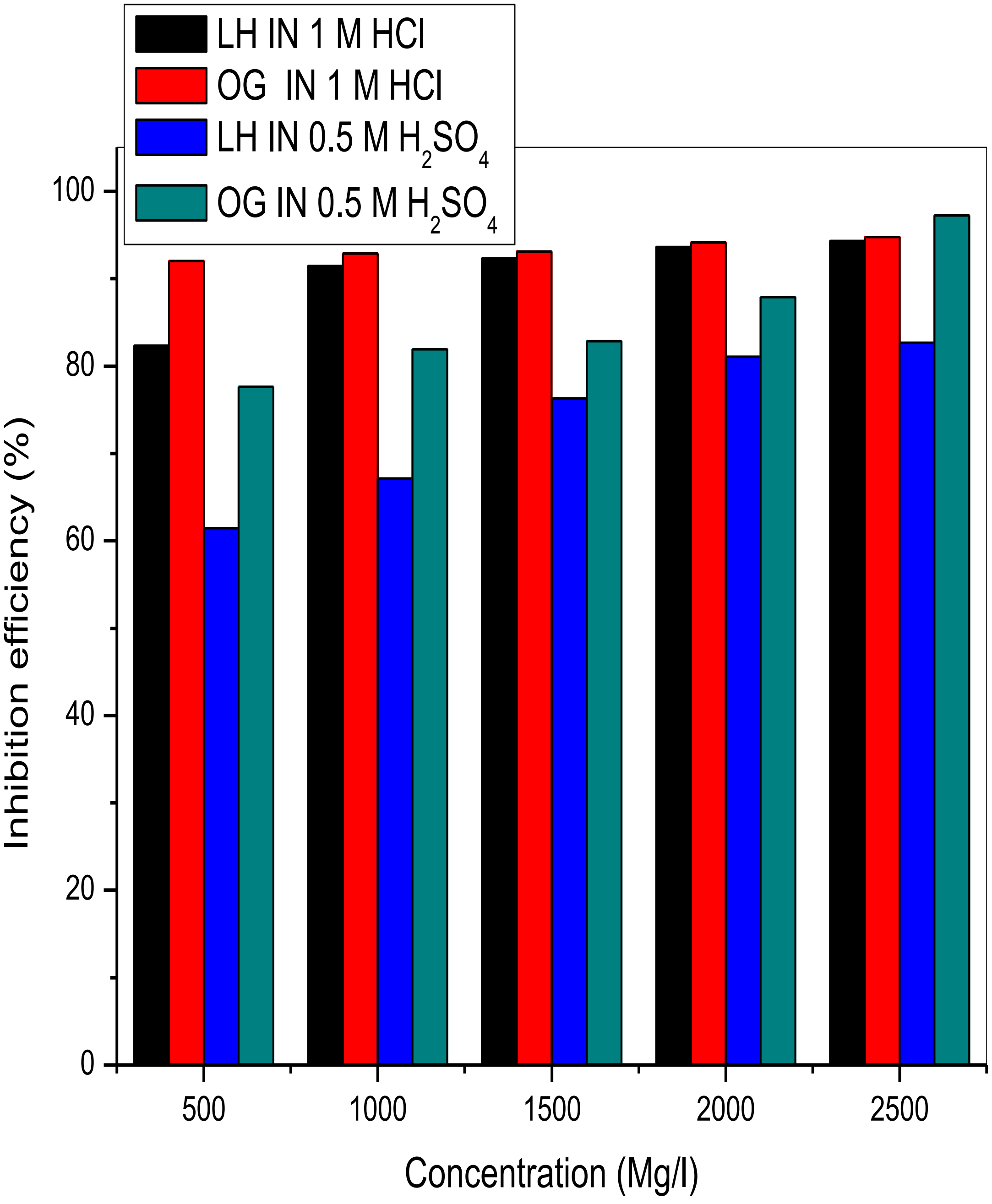

Figure 4.21 : Variation of Inhibition efficiency with various concentrations of LH and OG in 1M HCl and 0.5 M H_2SO_4 after twelve days.

Inhibition efficiency increased with increase in concentration of the aqueous extracts of LH and OG in both teat media.

4.2.4. VARIATION OF INHIBITION EFFICIENCY WITH IMMERSION TIME OF MILD STEEL CORROSION IN 1M HCL AND 0.5 M H_2SO_4 IN THE PRESENCE OF AQUEOUS EXTRACT OF LH AND OG

Experimental results as shown in tables **4.1- 4.28** above and figures **4.21 – 4.24** below reveals that inhibition efficiency increased with immersion time of mild steel in the presence of aqueous extracts of LH and OG in both test media. Highest inhibition efficiency of 97.27% and 94.31% was recorded after twelve days while lowest inhibition efficiency was recorded after three hours in LH and OG in both test media. The effect can be attributed to the fact that at longer immersion time the phytoconsistuents present are more adsorbed and forms stronger co - ordinate bond with the metal surface at the metal solution interphase, formation of the insoluble protective film of organic complex is thus more enhanced resulting to greater surface coverage, hence, inhibition efficiency increases.

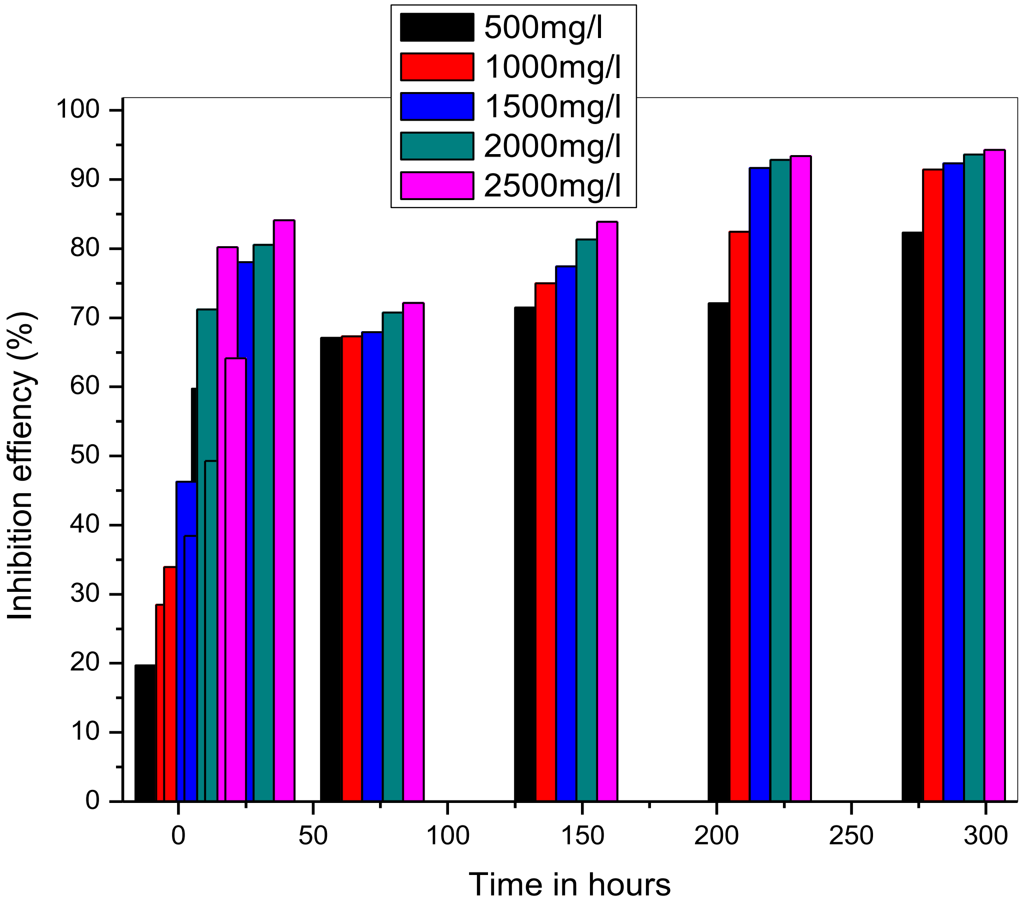

Figure 4.22 Variation of Inhibition efficiency with time of immersion of mild steel in 1 M HCl with and without aqueous extract of LH

Inhibition efficiency also increased with increase in immersion time of the test specimen in the presence of the aqueous extracts of LH and OG in both test media, highest inhibition efficiency was recorded after twelve days while lowest inhibition efficiency was recorded after three hours.

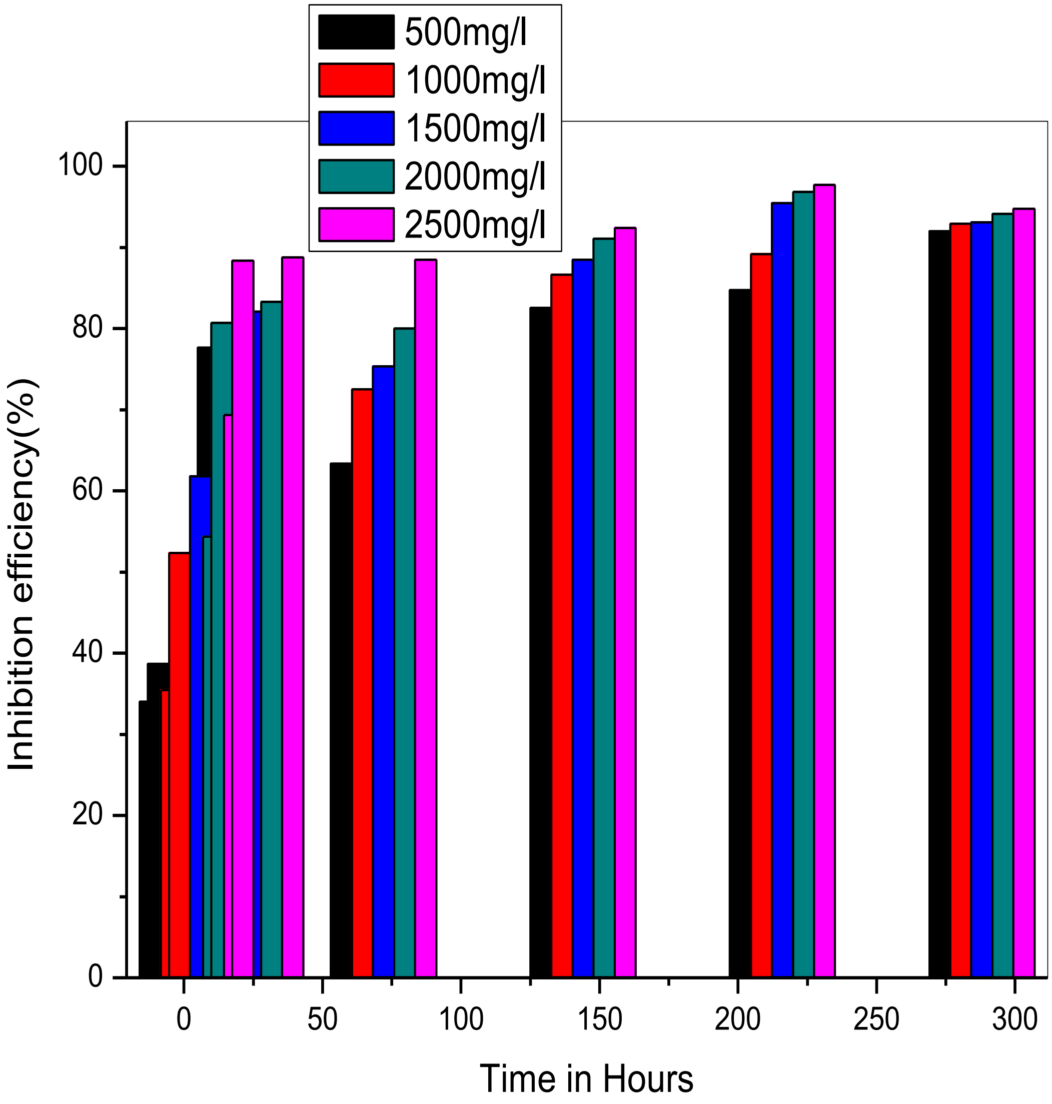

Figure 4.23 Variation of inhibition efficiency with time of immersion of mild steel in 1 M HCl with and without aqueous extract of OG

Inhibition efficiency also increased with increase in immersion time of the test specimen in the presence of the aqueous extracts of LH and OG in both test media, highest inhibition efficiency was recorded after twelve days while lowest inhibition efficiency was recorded after three hours.

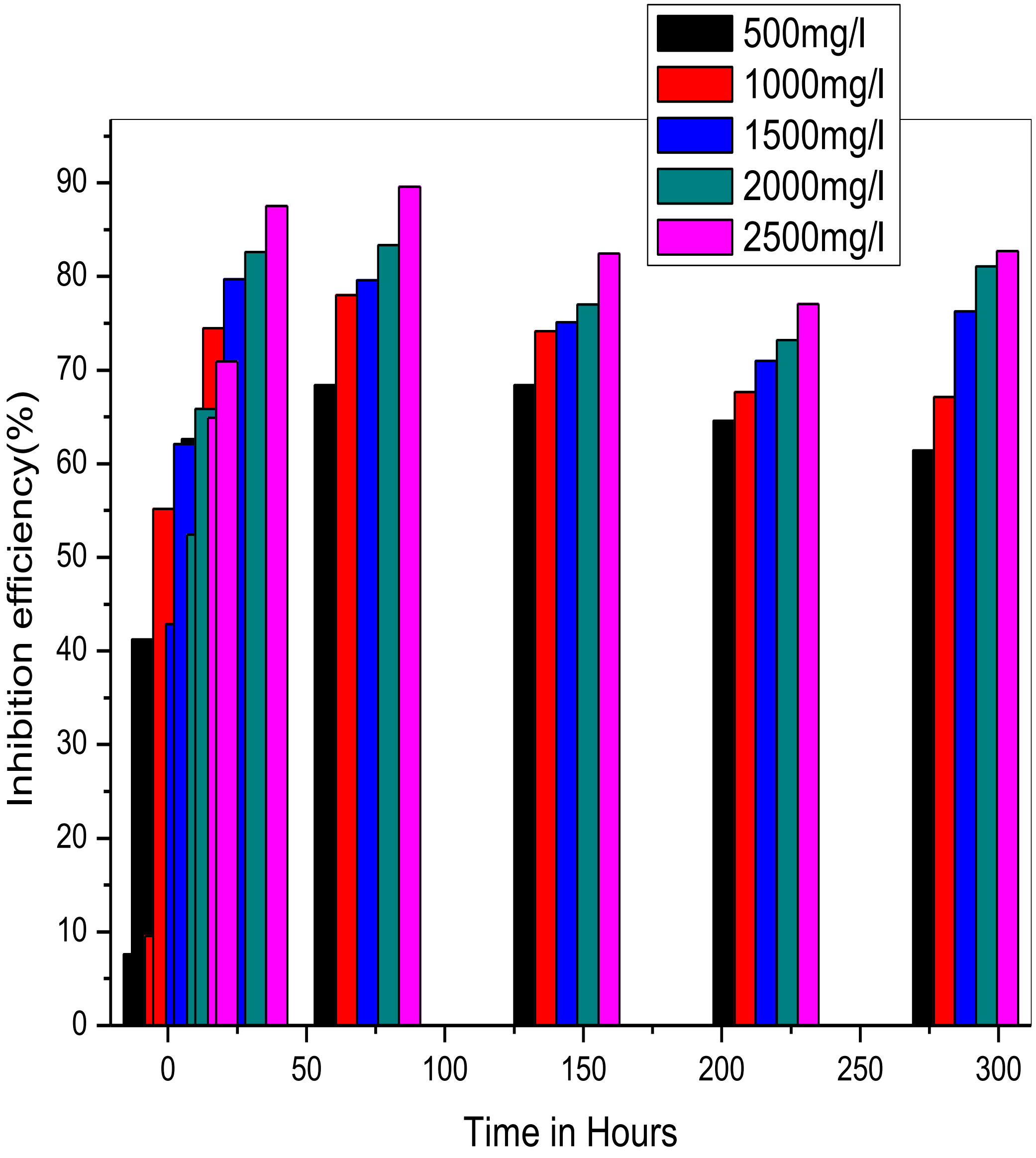

Figure 4.24: Variation of Inhibition efficiency with time of Immersion of mild steel in 0.5 M H_2SO_4 with and without aqueous extract of LH

Inhibition efficiency also increased with increase in immersion time of the test specimen in the presence of the aqueous extracts of LH and OG in both test media, highest inhibition efficiency was recorded after twelve days while lowest inhibition efficiency was recorded after three hours.

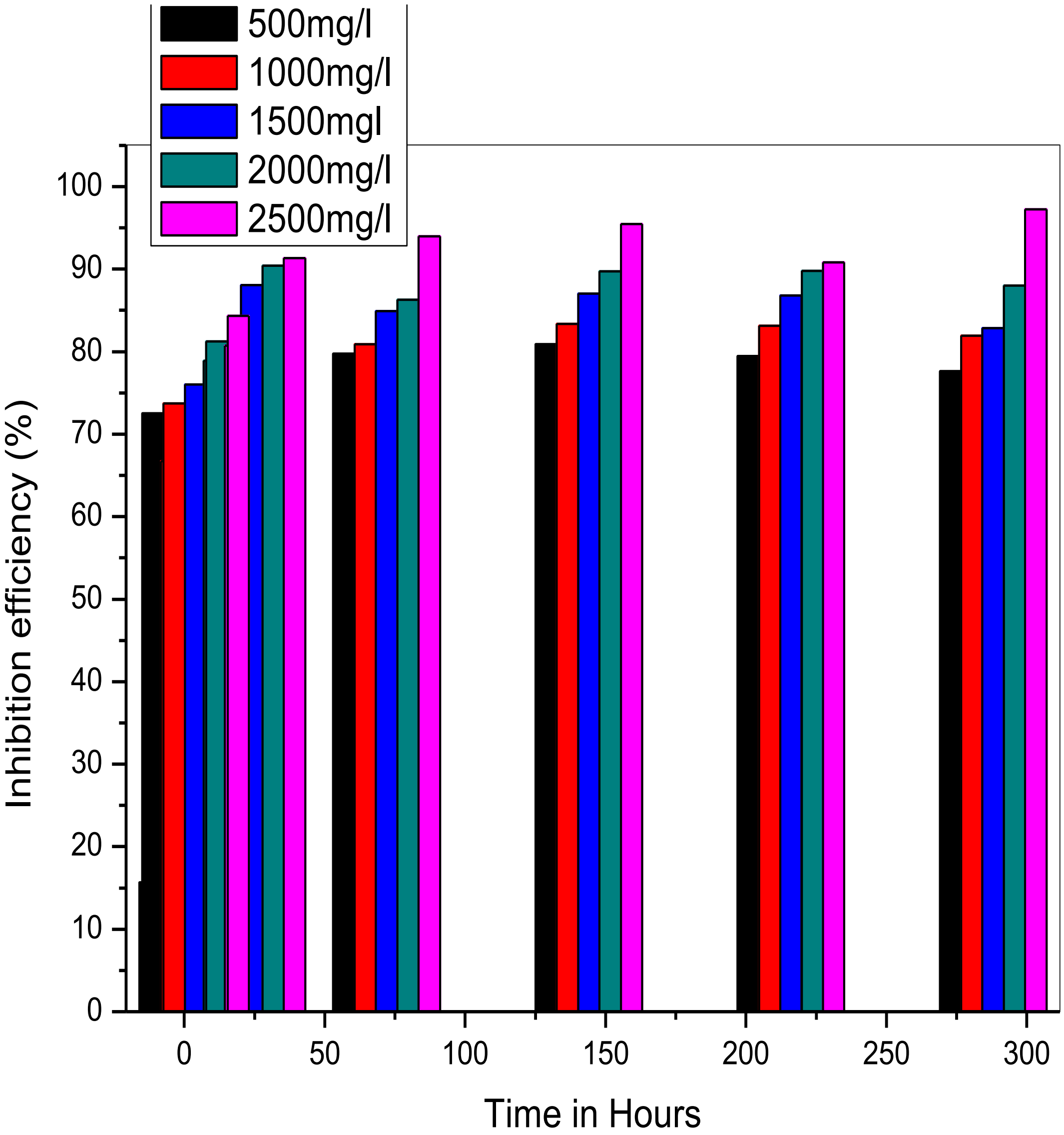

Figure 4.25 : Variation of Inhibition efficiency with time of immersion of mild steel in 0.5 M H_2SO_4 with and without aqueous extract of OG

Inhibition efficiency also increased with increase in immersion time of the test specimen in the presence of the aqueous extracts of LH and OG in both test media, highest inhibition efficiency was recorded after twelve days while lowest inhibition efficiency was recorded after three hours.

4.3 Effect of Temperature

Temperature studies was carried out on the corrosion inhibition of mild steel in 1 M HCl and 0.5 M H_2SO_4 in the presence of aqueous extracts of LH and OG within temperature ranges of 313 K -333 K to investigate temperature effect on the corrosion rate and inhibition performance of the mild steel in the presence of the aqueous extracts of LH and OG and determine the possible mechanism of the adsorption process .

4.3.1 Effect of temperature on corrosion rate .

Result from temperature studies carried out within the temperature range of **313 K – 333 K** is shown in tables **4.29 – 4.40** below**,** the results obtained reveals an increase in corrosion rate with rise in temperature of the test specimen in both test media in the presence and absence of LH and OG. Highest corrosion rate was recorded at 333 K in the absence of both plant extracts. The effect is expected because as the temperature increases the rate of corrosion of mild steel increases due to increase in the average kinetic energy of the reacting molecules. However corrosion rate decreased in the presence of both plant extract than in their absence which is due to the mitigating effect of the plant extracts on the corrosion rate of the mild steel.

4.3.2. Effect of temperature on inhibition efficiency.

Result obtained as shown in tables **4.29 – 4.40** below reveals an increase in inhibition efficiency of the test specimen with rise in temperature from 313 K to 323 K followed by a slight decrease at 333 K in 1 M HCl in the presence of OG and LH. From the data it can be inferred that the protective layer of the organic complex compound formed on the mild steel surface was more stable at 323 K after which there may be desorption of the plant extracts at 333 K hence the slight depletion in inhibition efficiency observed at 333 K. Similar results were obtained from

(Priya *et al.*, 2011; Vasuldha *et al.,* 2013; Sheeja *et al.,* 2014). However it was observed that inhibition efficiency of the test specimen decreased with rise in temperature in 0.5 M H_2SO_4 in the presence of both plant extract. This might be attributed to the desorption of the plant extract on the mild steel surface as the temperature rises from 313 K to 333 K.

Table 4.29: Results showing effect of temperature on the corrosion rate and inhibition performance of mild steel corrosion in 0.5 M H_2SO_4 with and without aqueous extract of LH at 313 K after three hours.

System Mg/l	Initial Weight(g)	Final weight(g)	Weight loss(g)	Average Weight loss(g)	Corrosion rate (g/cm^{2}hr)	Inhibition efficiency(%)
Blank						
A	4.7563	3.4914	1.2649	1.30795	62.60	-------
B	4.9633	3.6123	1.3510			
500mg/l						
A	4.8168	4.2410	0.5758	0.5760	27.57	55.96
B	4.6429	4.0667	0.5762			
2500mg/l						
A	4.5192	4.3357	0.1335	0.1398	6.691	89.31
B	4.9014	4.7553	0.1461			

Table 4.30 Results of temperature studies on the corrosion inhibition of mild steel in 0.5 M H_2SO_4 with and without aqueous extract of LH at 323 K after three hours

System Mg/l	Initial Weight(g)	Final Weight(g)	Weight loss(g)	Average weight loss	Corrosion Rate (g/cm^2hr)	Inhibition efficiency(%)
Blank						
A	3.3146	1.0141	2.3005	2.3334	177.62	--------
B	3.4050	1.0388	2.3662			
500mg/l						
A	4.6059	2.6780	1.9279	1.7559	84.04	52.68
B	4.5346	2.9507	1.5839			
2500mg/l						
A	4.6889	4.2350	0.4539	0.4959	23.76	86.64
B	4.8635	4.3256	0.5379			

Table 4.31: Results of temperature studies on the corrosion inhibition of mild steel in 0.5 M H_2SO_4 with and without aqueous extract of LH at 333 K after three hours

System mg/l	Initial Weight(g)	Finial Weight(g)	Weight Loss(g)	Average Weight loss(g)	Corrosion Rate (g/cm^{2}hr)	Inhibition efficiency(%)
Blank						
A	4.5150	0.0000	4.5150	4.6319	221.70	---------
B	4.7487	0.0000	4.7487			
500mg/l						
A	4.9586	2.5361	2.4225	2.5112	120.20	45.76
B	4.8188	2.2174	2.6014			
2500mg/l						
A						
B	4.6248	4.0676	0.5572	0.64015	30.64	86.18
	4.9254	4.2023	0.7231			

Table 4.32: Results of temperature studies on the corrosion inhibition of mild steel in 0.5 M H_2SO_4 with and without aqueous extract of OG at 313 K after three hours

System mg/l	Initial Weight (g0	Final Weight (f0	Weight loss(g)	Average weight loss(g)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank						
A	4.7563	3.4941	1.2649	1.30795	62.60	====
B	4.9633	3.6123	1.3510			
500mg/l						
A	4.7953	4.5835	0.2118	0.21845	10.46	83.30
B	5.2124	4.9873	0.2251			
2500mg/l						
A	4.6366	4.5713	0.0653	0.07825	3.75	94.02
B	5.1512	5.0600	0.0912			

Table 4.33 : Results of temperature studies on the corrosion inhibition of mild steel in 0.5 M H_2SO_4 with and without aqueous extract of OG at 323 K after three hours

.

System mg/l	Initial weight (g)	Final Weight (g)	Weight Loss(g)	Average weight loss(g)	Corrosion Rate (g/cm^{2}hr)	Inhibition efficiency (%)
Blank						
A	4.6631	1.2259	3.4372	3.71095	177.62	--------
B	4.6849	0.7002	3.9847			
500mg/l						
A	4.8748	3.3711	1.5037	1.52435	72.96	58.92
B	4.7456	3.2006	1.5450			
2500mg/l						
A	4.8040	4.5907	0.2133	0.2254	10.79	93.93
B	4.7622	4.5247	0.2375			

Table 4.34: Results of temperature studies on the corrosion inhibition of mild steel in 0.5 M H_2SO_4 with and without aqueous extract of OG at 333 K after three hours.

System	**Initial weight (g)**	**Final weight (g)**	**Weight loss(g)**	**Average weight loss(g)**	**Corrosion rate (g/cm^2hr)**	**Inhibition Efficiency(%)**
Blank						
A	4.5150	0.0000	4.5150	4.63185	221.70	------
B	4.7487	0.0000	4.7487			
500mg/l						
A	4.8194	2.6113	2.2081	2.3055	110.35	50.22
B	4.8304	2.4274	2.4030			
2500mg/l						
A	4.6398	4.2443	0.3955	0.38015	18.20	91.79
B	4.7460	4.3812	0.3648			

Table 4.35 : Results of temperature studies on the corrosion inhibition of mild steel in 1 M HCl with and without aqueous extract of LH at 313 K after three hours.

System mg/l	Initial Weight (g)	Final Weight (g)	Weight loss(g)	Average weight Loss(g)	Corrosion Rate (g/cm^{2}hr)	Inhibition Efficiency (%)
Blank						
A	5.1963	4.8668	0.3295	0.33645	16.10	-------
B	4.8975	4.55410	0.3434			
500mg./l						
A	4.6542	4.5102	0.0640	0.0642	3.07	80.92
B	5.1978	5.1334	0.0644			
2500mg/l						
A	4.7897	4.7671	0.0226	0.02535	1.21	92.46
B	5.0180	4.9899	0.0281			

Table 4.36: Results of temperature studies on the corrosion inhibition of mild Steel in 1 M HCl with and without aqueous extract of LH at 323 K after three hours.

System mg/l	Initial Weight(g)	Final weight(g)	Weight loss(g)	Average weight loss(g)	Corrosion rate (g/cm^{2}hr)	Inhibition efficiency(%)
Blank						
A	4.66123	3.4917	1.6646	1.4802	70.85	
B	4.4977	3.2631	1.2958			
500mg/l						
A	4.8928	4.6165	0.2793	0.2333	11.16	85.24
B	4.3505	4.1633	0.1872			
2500mg/l						
A	5.0687	5.0073	0.0614	0.0646	3.09	95.54
B	4.7114	4.6436	0.0678			

Table 4.37: Results of temperature studies on the corrosion inhibition of mild steel in 1 M HCl with and without aqueous extract of LH at 333 K after three hours .

System	Initial weight (g)	Final Weight(g)	Weight loss(g)	Average weight loss(g)	Corrosion rate (g/cm^{2}hr)	Inhibition efficiency(%)
Blank						
A	4.7884	2.1938	2.5946	2.6496	126.82	
B	4.9562	2.2516	2.7046			
500Mg/l						
A	4.6870	3.5591	1.1279	1.2139	58.10	54.18
B	4.8758	3.5759	1.2999			
2500mg/l						
A	4.8763	4.7254	0.1509	0.13685	6.55	94.83
B	4.7539	4.6311	0.1228			

Table 4.38 : Results of temperature studies on the corrosion inhibition of mild steel in 1 M HCl with and without aqueous extract of OG at 313 K after three hours

System	Initial weight(g)	Final weight(g)	Weight loss(g)	Average weight loss(g)	Corrosion rate (g/cm^{2}hr)	Inhibition efficiency(%)
Blank						
A	5.1963	4.8668	0.3295	0.33645	16.10	
B	4.8975	4.5541	0.3434			
500mg/l						
A	5.0233	4.9844	0.0898	0.0698	3.08	80.87
B	4.9755	4.9257	0.0498			
2500mg/l						
A	5.1656	5.1498	0.0158	0.01495	0.72	95.56
B	4.6653	4.6512	0.0141			

Table 4.39 : Results of temperature studies on the corrosion inhibition of mild steel in 1 M HCl with and without aqueous extract of OG at 323 K after three hours.

System	Initial weight(g)	Final weight(g)	Weight loss(g)	Average weight loss(g)	Corrosion rate (g/cm^2hr)	Inhibition efficiency(%)
Blank						
A	4.9277	3.4917	1.6646	1.4802	70.85	
B	4.5589	3.2631	1.2958			
500mg/l						
A	4.5087	4.4063	0.1024	0.11325	5.42	92.55
B	4.9970	4.8729	0.1241			
2500mg/l						
A	4.5620	4.5190	0.0430	0.04295	2.06	97.60
B	4.7227	4.6798	0.0429			

Table 4.40 : Results of temperature studies on the corrosion inhibition of mild steel in 1 M HCl with and without aqueous extract of OG at 333 K after three hours.

System	Initial weight(g)	Finial weight(g)	Weight Loss(g)	Average weight loss(g)	Corrosion rate (g/cm^{2}hr)	Inhibition Efficiency(%)
Blank						
A	4.7884	2.1938	2.5946	2.6496	126.82	
B	4.9562	2.2516	2.7046			
500mg/						
A	4.7522	4.3125	0.4397	0.4618	22.10	82.57
B	4.6569	4.1730	0.4839			
2500g/l						
A	4.8603	4.7802	0.0801	0.0733	3.51	97.23
B	4.6154	4.5489	0.0665			

4.4. Thermodynamic Studies .

Temperature studies gives an insight on the possible mechanism of the inhibition process, the variation of inhibition efficiency with temperature tables **4.29 – 4.40** above and the apparent activation energies of the inhibition process table **4.41** helps to predict the mechanism of the adsorption process. In general two types of adsorption mechanism can be used to describe the adsorption of an organic species on a corroding metal specimen namely: physical adsorption or physisorption and chemical or chemisorption, in the former the inhibiting molecules are physically attached to the metal specie via weak van der waals forces of attraction (Popova *et al.*, 2003). The physisorped molecules are attached at the cathodic site, retarding metal dissolution by reducing rate of cathodic reaction. In chemisorption or chemical adsorption the inhibiting molecules are attached to the corroding metal specie via strong chemical bonds, the chemisorbed molecules are attached at the anodic site thus inhibiting the dissolution of the metal species. It has been suggested that the most efficient inhibitor is one which inhibits the anodic site by chemisorption.

4.4.1 Activation Energy E_a.

The activation energy of the process was calculated from the Arrhenius equation stated in equation **11** above. Results of the activation energies of the adsorption process of both inhibitors in the two different test media are given in the table **4.41** below

Table : 4.41: Ea values of the corrosion inhibition of mild Steel in 1 M HCl and 0.5 M H_2SO_4 in the presence of aqueous extract of OG and LH at temperature ranges of 313 K - 333 K

System	Ea of Specimen in 1 M HCl in the presence of LH	Ea of specimen in 0.5 M H_2SO_4 in the presence of LH	Ea of specimen in 1 M HCl in the presence of OG	Ea of specimen in 0.5 M H_2SO_4 in the presence of OG
Blank	89.37 KJm^{-1}	54.76 kJm^{-1}	89.37 KJm^{-1}	54.76KJm^{-1}
500mg/l	127.33KJm^{-1}	63.75 KJm^{-1}	101.51 KJm^{-1}	102 KJm^{-1}
2500mg/l	73.13KJm^{-1}	65.89 KJm^{-1}	68.60 KJ m^{-1}	68 KJm^{-1}

Results obtained revealed that activation energy values in the presence of aqueous extract of LH and OG at both 500 Mg/l and 2500 Mg/l in 0.5 M H_2SO_4 were higher than in the blank solution (i.e in the absence of the extracts) whereas activation energy values of the adsorption process in 1 M HCl were lower at 2500 Mg/l of OG and LH than in their absence and higher at 500 Mg/l of OG and LH than in their absence. It has been suggested that a decrease in inhibition efficiency with rise in temperature followed by analogous increase in corrosion activation energy in the presence of the inhibitor compared to its absence can be attributed to physical adsorption of the organic molecules on the metal surface, on the other hand an increase in inhibition efficiency with rise temperature followed by a corresponding decrease in corrosion activation energy in the presence of the inhibitor than in the absence suggests chemisorption of the inhibiting molecules on the corroding metal specie. Results obtained from the study suggests physisorption of the inhibiting species in 0.5 M H_2SO_4 at both 500 Mg/l and 2500 Mg/l concentrations of OG and LH respectively, activation energy values were found to be 63.75 KJm^{-1} and 65.78 KJm^{-1} in the presence of LH, 102 KJm^{-1} and 68 KJm^{-1} in the presence of OG and 54.76 KJm^{-1} in the absence of both inhibitors while inhibition efficiency decreased in this order 83.30% < 58.92% < 50.22% at 500mg/l ; 94.02% < 93.93% < 91.79% at 2500mg/l and 55.96% < 52.68% < 45.76% at 500mg/l; 89.31% < 86.64% < 86.18% at 2500 mg/l in OG and LH respectively. On the other hand, physisorption mechanism was favoured at 500 Mg/l concentrations of both inhibitors in 1 M HCl, activation energy values was found to be 127.33 KJm^{-1} and 101.51 KJm^{-1} in the presence of LH and OG respectively and 89.37 KJm^{-1} in their absence. However, chemisorption was favoured at 2500 Mg/l of OG and LH in I M HCl , activation energy values was found to be 73.13 KJm^{-1} and 68 KJm^{-1} in LH and OG respectively and 89.37 $KJm-^{1}$ in their absence, hence it can be suggested that the mechanism of adsorption is via physisorption and chemisorption but predominantly of physisorption. The results are in excellent agreement with the works of (Abiola *et al.,* 2007; Ebenso *et al.,* 2007; Oguzie *et al.,* 2010).

4.4.2 Gibb’s Free Energy

Gibb’s free energies of the reaction was calculated using the relationship between the equilibrium constant of water extract of OG and LH expressed mathematically in equation **12** above. Results obtained are given in the table below:

Table 4. 42 : ΔG values of the corrosion of mild steel in 0.5 M H_2SO_4 in the presence of aqueous extract of LH and OG at temperature ranges of 313 K - 333 K

Temperature in K	**ΔG of LH in 0.5M H_2SO_4 at low concentration**	**ΔG of LH in 0.5M H_2SO_4 at high concentration**	**ΔG of OG in 0.5 M H_2SO_4 at low concentration**	**ΔG of OG in 0.5 M H_2SO_4 at high concentration**
313	-12.88KJm^{-1}	-13.59KJm^{-1}	-16.44KJm^{-1}	-15.24KJm^{-1}
323	-12.94KJm^{-1}	-13.35KJm^{-1}	-13.62KJm^{-1}	-15.68KJm^{-1}
333	-12.57KJm^{-1}	-13.65KJm^{-1}	-13.07KJm-1	-12.73kjm^{-1}

Table 4.43 : ΔG values of the corrosion of mild steel 1M HCL in the presence of aqueous extract of OG and LH at 313 K – 333 K

Temperature in K	**ΔG values of LH in 1M HCl at low concentration**	**ΔG values of LH in 1M HCL at high concentration**	**ΔG values of OG in 1M HCl at low concentration**	**ΔG values of OG in 1M HCl at high concentration**
313	-16.02KJm^{-1}	-14.59KJm^{-1}	-17.16kJm-1	-16.06KJm^{-1}
323	-17.36KJm^{-1}	-16.56KJm^{-1}	-19.42kJm-1	-18.28KJm-1
333	-13.50KJm^{-1}	-16.64KJm^{-1}	-17.35KJm-1	-18.44KJm^{-1}

The negative values of ΔG ensures spontaneity of the adsorption process and stability of the adsorbed layer on the mild steel surface. In general ΔG values of -20 KJm^{-1} or lower are consistent with physisorption while those around -40 KJm^{-1} or higher involves charge sharing transfer from organic molecules to the metal surface to form co – ordinate type of bond indicating chemisorption (Ebenso *et al.,* 2003; Umoren *et al.*, 2009; Tao *et al.,* 2010). Results obtained shows that ΔG values are negative in all cases and less than -20 KJm^{-1}, this is consistent with literature therefore authenticates physical adsorption and agrees with the works of (Liang *et al.*, 2011). This implies that the plant extracts adheres on the corroding metal and gives a very strong inhibitor.

4.4.3 Heat of Adsorption Q_{ads}

The energy of adsorption which is approximately equal to enthalpy change or change in heat content of reaction ΔH_{ads} was obtained using the trend of change in degree of surface coverage with temperature stated mathematically in equation **13** above. The table below shows the values of ΔH_{ads} of the adsorption process:

Table 4.44 : ΔH_{ads} values of the corrosion of mild steel in !M HCl and 0.5M H_2SO_4 in the presence of aqueous extracts of OG and LH at 313 K – 333 K

System	ΔH_{ads} values of OG in 1 M HCl	ΔH_{ads} values of OG in 0.5 M H_2SO_4	ΔH_{ads} values of LH in 1 M HCl	ΔH_{ads} values of LH in in 0.5 M H_2SO_4
500mg/l	4.93KJm^{-1}	-69.26KJm^{-1}	44.42KJm^{-1}	-17.74KJm^{-1}
2500mg/l	21.16KJm^{-1}	-14.73KJm^{-1}	17.44KJm^{-1}	-12.67KJm^{-1}

Results obtained as shown in tables **4.44** above reveals that ΔH_{ads} of the adsorption process is negative in 0.5 M H_2SO_4 and positive in 1 M HCl in both extracts respectively. In general negative value of ΔH_{ads} reflects exothermic reaction which implies that inhibition efficiency decreases with rise in temperature, on the other hand, ΔH_{ads} positive is an indication of an endothermic reaction reflecting that inhibition efficiency increases with rise in temperature. Also, ΔH_{ads} values less than $80KJm^{-1}$ indicates a physical adsorption mechanism (Atkins, 1998). Thus results from the study indicates an exothermic and endothermic reaction occurring in the adsorption of both extract in 0.5 M H_2SO_4 and 1 M HCl respectively, also ΔH_{ads} values were less than $80KJm^{-1}$ in all cases which is an indication that adsorption process is through physisorption mechanism.

4.5 Analysis of Result from potentiodynamic polarization measurements

Results of the potentiodynamic polarization measurement obtained for the anodic and cathodic polarization of mild steel corrosion in 1 M HCl and 0.5 M H_2SO_4 with and without the various concentration of LH and OG as shown in figures **4.25 – 4.28** above reveals the shape of the polarization curve and the electrochemical corrosion kinetic parameters obtained from tafel plot given in tables **4.45 – 4.48** shows that both anodic and cathodic reactions are inhibited in the presence of the aqueous extract of LH and OG in both test media. E_{corr} values slightly shifted towards both positive and negative direction in the presence of the extracts in both test media indicating that both extracts are of mixed type inhibitors. In addition, from figures **4.25 -4.28** below it is clearly observed that the plant extracts reduces anodic and cathodic current densities indicating the inhibiting effect of the extract (Vracar *et al.,* 2002). Addition of the aqueous extract of LH and OG in both test media retards the dissolution of the metal at the anode and the evolution of $H_2(g)$ at the cathode. Polarization results also showed that corrosion current density (I_{corr}) was lower at high concentration and higher at low concentration of LH and OG. This can be attributed to the increase in the block fraction of the metal surface by adsorption (Oguzie *et al.*,2010; Sharmila *et al.*,2010). The inhibition efficiency obtained from corrosion current density showed higher inhibition efficiency at high concentrations of LH and OG than at lower concentration. Results of potentiodyamic polarization on the corrosion inhibition of mild in 1 M HCl and 0.5 M H_2SO_4 in the presence of aqueous extracts of LH and OG is shown in tables **4.45 -4.48**

Table 4 .45: PDP Result of analysis on the corrosion of mild steel in 0.5 M H_2SO_4 with and without aqueous extract of OG.

Concentration	**I_{corr} (µA)**	**E_{corr} (Mv)**	**Inhibition Efficiency(%)**
Blank	591.3	-485.3	------
500mg/L	8.4	-515.3	98.6
2500mg/l	2.5	-511.02	99.6

Table 4.46: PDP Result of analysis on the corrosion of mild steel in 1 M HCl with and without aqueous extract of OG

Concentration mg/l	**I_{corr} (µA)**	**E_{corr} (Mv)**	**Inhibition Efficiency(%)**
Blank	259	-470.4	------
500	4.1	-525.4	98.4
2500	2.2	-487.5	99.1

Table 4.47: PDP Result of analysis of the corrosion of mild steel in 0.5M H_2SO_4 with and without aqueous extract of LH

Concentration mg/l	**I_{corr} (μA)**	**E_{corr} (Mv)**	**Inhibition Efficiency(%)**
Blank	591.3	-485.3	--------
500	5.0	-514.993	99.2
2500	1.9	-492.09	99.7

Table 4.48: PDP Result of analysis of the corrosion of mild steel in 1M HCl with and with aqueous extract of LH.

Concentration mg/l	**I_{corr} (µA)**	**E_{corr} (Mv)**	**Inhibition Efficiency(%)**
Blank	259	-470.4	--------
500	2.0	-489.3	99.2
2500	0.9	454.2	99.6

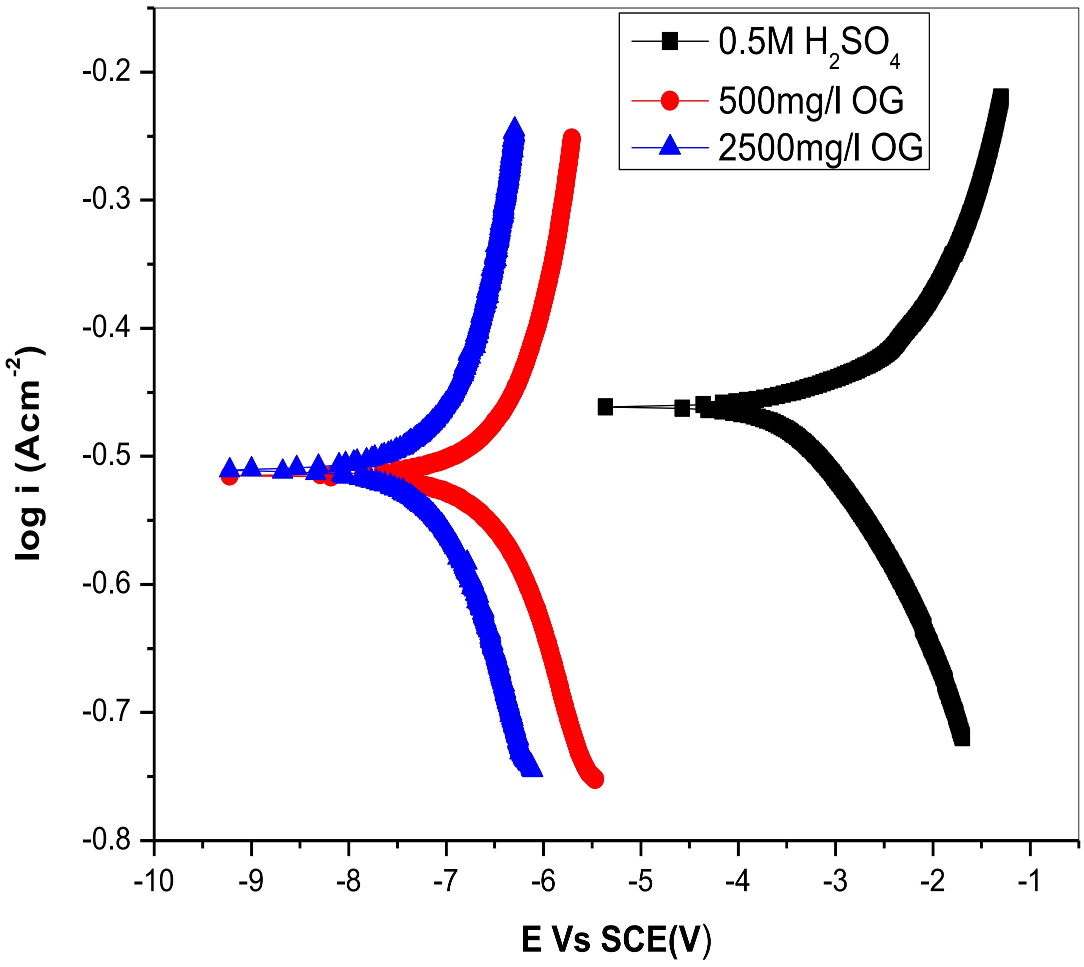

Figure 4.25 : Potentiodynamic polarization curve of mild steel in 0.5 M H_2SO_4 with and without aqueous extract of OG

Polarization curve obtained reveals that both the anodic (positive direction) and cathodic (negative direction) reaction are inhibited in the process with predominant cathodic effect, there was a slight shift in E_{corr}, This therefore implies that the inhibitor (OG) is of mixed type with predominant cathodic effect in 0.5 M H_2SO_4

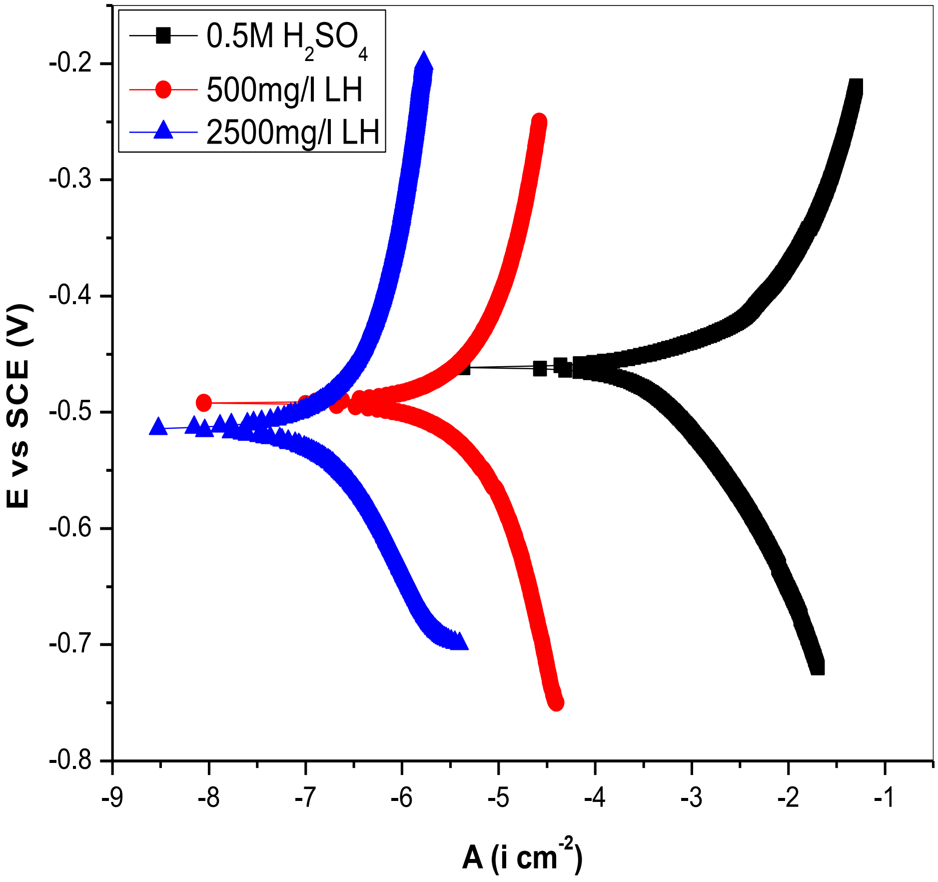

Figure 4.26: Potentiodynamic polarization curve of mild steel in 0.5 M H_2SO_4 with and without aqueous extract of LH

Polarization curve obtained reveals that both the anodic (positive direction) and cathodic (negative direction) reaction are inhibited in the process with predominant cathodic effect, there was a slight shift in E_{corr}, This therefore implies that the inhibitor (LH) is of mixed type with predominant cathodic effect in 0.5 M H_2SO_4

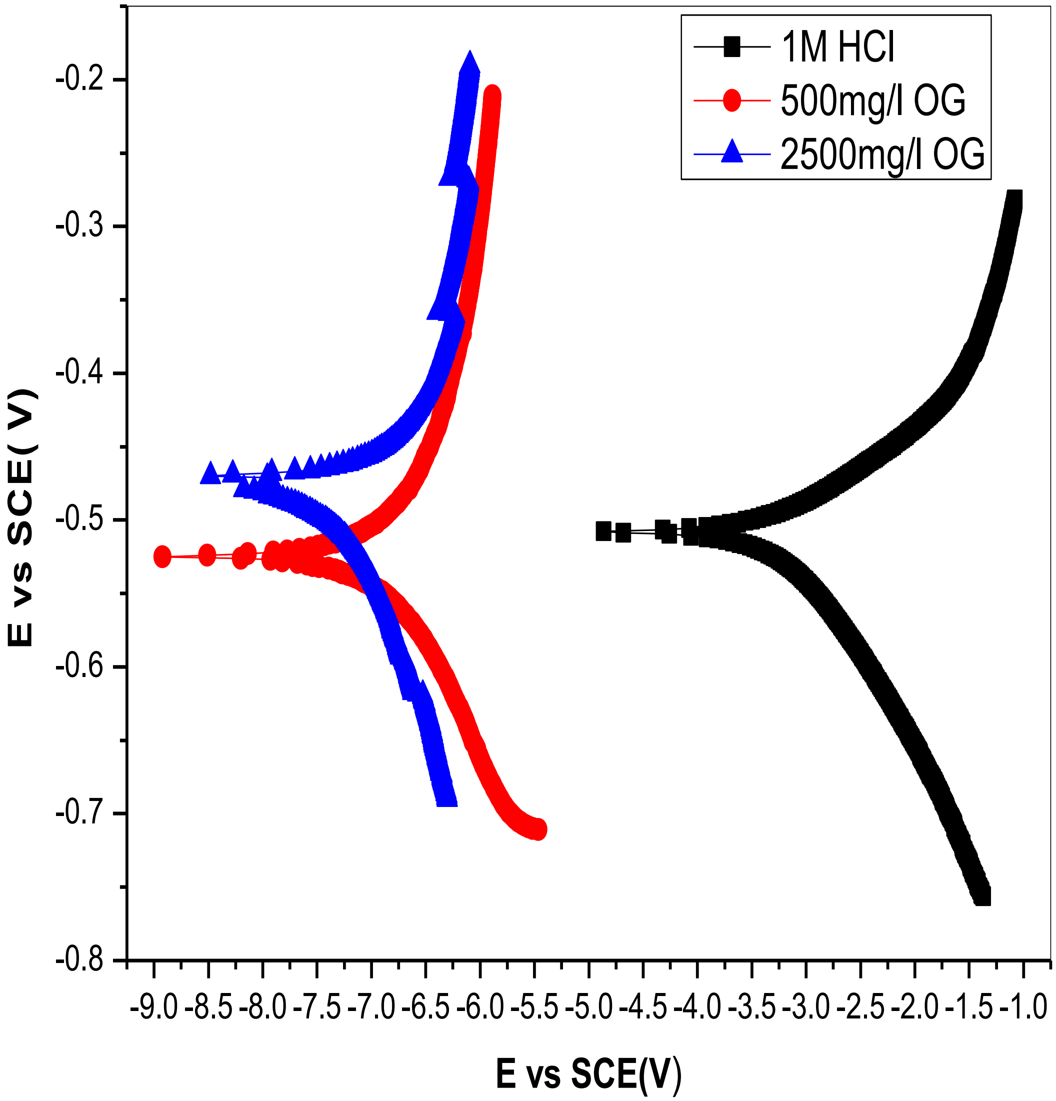

Figure 4.27: Potemtiodynamic polarization curve of mild steel in 1M HCl with and without aqueous extract of OG.

Polarization curve obtained reveals that both the anodic (positive direction) and cathodic (negative direction) reaction are inhibited in the process, there was a slight shift in E_{corr}. This therefore implies that the inhibitor (OG) is of mixed type .

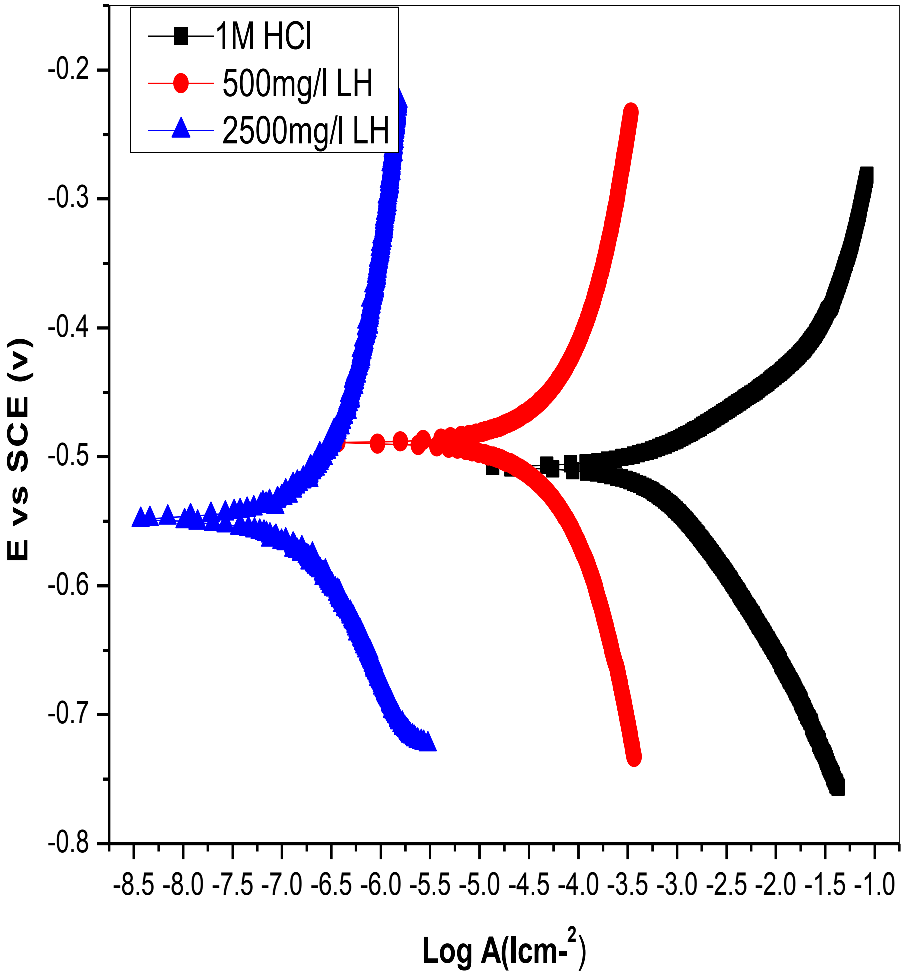

Figure 4.28: Potentiodynamic polarization curve of mild steel in 1M HCl with and without aqueous extract of LH

Polarization curve obtained reveals that both the anodic (positive direction) and cathodic (negative direction) reaction are inhibited in the process, there was a slight shift in E_{corr}. This therefore implies that the inhibitor (LH) is of mixed type .

4.6 Adsorption Considerations

Adsorption isotherms provides basic information about the interaction of the inhibitor on mild steel surface. It explains the mechanism of corrosion inhibition of organic inhibitor molecules from the aqueous phase (org) and water molecules (solution) associated with the metallic surface (H_20_{ads}), this can be represented by the following equilibrium (El – Etre, 2008; Negm *et al* 2012).

$$Org_{(soln.)} + H_20_{(ads)} \rightarrow Org_{(ads)} + XH_20 \quad (14)$$

where x is the number of water molecules replaced by one organic molecules. In the process the adsorption of the consistuents of *Landolphia heudelotii* and *Ocimum gratissimum* were accompanied by the desorption of water molecules, Cl^- and SO_4^{2-} ions from the mild steel surface. The extent of corrosion depends on the surface conditions and mode of adsorption of the inhibitor. In general inhibitors can function either by physical adsorption (physisorption) and Chemical adsorption (Chemisorption)

4.5.1 Physical adsorption:

This occurs when the force of attraction between adsorbate and adsorbent are Vander waals forces . It is also known as Vander waals adsorption. In physical adsorption the force of attraction between adsorbent and adsorbate are very weak thus can easily be reversed by heating or increasing the pressure.

4.5.2 Chemical adsorption

This occurs when the force of attraction existing between the adsorbate and adsorbent are almost the same in strength as chemical bonds, the adsorption is called chemical adsorption, it is also known as Langmuir adsorption. In chemisorption the force of attraction is strong therefore cannot be easily reversed (Moretti *et al.*, 1995)

Different adsorption isotherm such as Langmuir, Temkin , Frumkin, Freundlich ,Flory Huggins etc can be used to explain adsorption process. The adsorption isotherms describes the behaviour of the aqueous plant extract on mild steel surface. The correlation coefficient R^2 is used to choose the isotherm that best fits experimental data. In this work Langmuir adsorption was used to describe the adsorption process .

4.7 Langmuir Adsorption Isotherm

Langmuir in 1916 published a model isotherm for gases adsorbed on solid which retained its name. His isotherm was based on the assumption that all adsorption sites are equivalent and that particles occurs independently from nearby sites being occupied or not (Deng & Fu, 2012). The isotherm is based on four assumptions :

- The surface of the adsorbent is uniform, that is all adsorbed sites are equivalent
- Adsorbed molecules do not interact.
- All adsorption occurs through the same mechanism.
- At the maximum adsorption only monolayer is formed; molecules of adsorbate do not deposit on other already adsorbed adsorbate, only on free surface of the adsorbent.

The mechanism can be illustrated using the equation below :

$$X_{(g)} \quad + \quad Y_{(s)} \quad \overset{\textbf{adsorption}}{\underset{\textbf{desorption}}{\leftrightarrow}} \quad XY \tag{15}$$

Where $X_{(g)}$ unadsorbed gaseous molecules, $Y_{(s)}$ unoccupied metal surface and XY adsorbed gaseous molecules .

The degree of surface coverage (θ) values for different concentration of the inhibitor in 1 M HCl and 0.5 M H_2SO_4 have been evaluated from weight loss data and is shown in tables **4.49 – 4.52** (Morettif & Guidi, 2002) using the mathematical model shown below

$$\Theta = 1.E(\%)/100 \qquad (16)$$

Where θ is the degree of surface coverage and 1.E(%) is the percentage inhibition efficiency. A correlation between surface coverage (θ) and the concentration (C) of the inhibitor in the electrolyte can be represented by Langmuir adsorption isotherm as follows (Satapathy *et al.*, 2009):

$$C/\theta = 1/K + C \qquad (16)$$

Where K is the adsorption equilibrium constant , θ is the degree of surface coverage. Plots of C/Θ versus C is a straight line with slope close to unity and linear correlation co-efficient approximately equal to 0.95, is a good fit thus adheres to Langmuir adsorption isotherm. From the results of analysis plots of C/Θ against concentration shown in figures **4.29 – 4.32** below is a straight line graph, the slopes of the graphs are close to unity and values of linear correlation coefficient as shown table **4.53** below are all above 0.95 indicating that the adsorption of *Landolphia heudelotii* and *Ocimum gratissimum* extract on mild steel surface in both acidic media at different immersion periods well fits Langmuir adsorption isotherm. Due to the unknown molecular mass of *Landolphia heudelotii* and *Ocimum gratissimum* extract, the energy of adsorption and thermodynamic parameters cannot be calculated (Oguzie, 2006). Tables **4.49 – 4.52** below shows values of inhibition efficiency, degree of surface coverage (Θ), C/Θ for the Langmuir adsorption isotherm on the adsorption of LH and OG on mild steel while tables

4.53 shows values of the slopes and linear correlation coefficient, R^2 obtained from the graph of C/θ against θ.

Table 4.49 : Inhibition efficiency, degree of surface coverage of corrosion inhibition of mild steel in 1 M HCl at different concentration of LH in different periods of immersion

Periods of Immersion	Concentration	Inhibition Efficiency	Surface Coverage(θ)	C/θ
72 hours	500	67.09	0.6709	745.27
	1000	67.30	0.6730	1491.87
	1500	67.92	0.6792	2208.48
	2000	70.78	0.7078	2825.66
	2500	72.16	0.7216	3464.52
144 hours	500	71.48	0.7148	690.47
	1000	75.00	0.7500	1333.33
	1500	77.49	0.7749	1935.73
	2000	81.32	0.8132	2459.42
	2500	83.88	0.8388	2980.45
216 hours	500	72.08	0.7208	693.67
	1000	82.45	0.8245	1212.86
	1500	91.68	0.9168	1636.13
	2000	92.82	0.9282	2154.71
	2500	93.40	0.9340	2676.66
288 hours	500	82.33	0.8233	607.31
	1000	91.46	0.9146	1093.37
	1500	92.32	0.9232	1624.78
	2000	93.62	0.9362	2136.30
	2500	94.31	0.9431	2650.83

Table 4.50 : Inhibition efficiency, degree of surface coverage of corrosion inhibition mild Steel in 0.5 M H_2SO_4 at different concentrations of LH in different periods of immersion

Periods	Concentration	Inhibition Efficiency	Degree of Surface Coverage(ө)	C/ө
72 hours	500	68.40	0.6840	730.99
	1000	78.00	0.7800	1282.05
	1500	79.58	0.7958	1884.90
	2000	83.37	0.8337	2398.94
	2500	89.61	0.8961	2789.87
144 hours	500	68.40	0.6840	730.99
	1000	74.14	0.7414	1348.50
	1500	75.13	0.7513	1996.54
	2000	77.01	0.7701	2597.07
	2500	82.46	0.8246	3031.77
216hours	500	64.60	0.6460	773.99
	1000	67.64	0.6764	1483.68
	1500	71.00	0.7100	2112.68
	2000	73.18	0.7318	2732.99
	2500	77.07	0.7707	3243.80
288hours	500	61.43	0.6143	813.93
	1000	67.13	0.6713	1489.65
	1500	76.28	0.7628	1966.44
	2000	81.07	0.8107	2467
	2500	82.70	0.8270	3022.97

Table: 4.51 : Inhibition efficiency, degree of surface coverage of corrosion inhibition mild steel in 1 M HCl at different concentration OG in different periods of immersion.

Periods	Concentration	Inhibition Efficiency	Degree of Surface Coverage(ɵ)	C/ɵ
72 hours	500	63.35	0.6335	789.26
	1000	72.53	0.7253	1378.74
	1500	75.36	0.7536	1990.44
	2000	80.00	0.8000	2500.00
	2500	88.47	0.8847	2825.82
144 hours	500	82.55	0.8255	605.69
	1000	86.66	0.8666	1153.93
	1500	88.52	0.8852	1694.53
	2000	91.08	0.9108	2195.87
	2500	92.40	0.9240	2705.63
216 hours	500	84.74	0.8474	590.04
	1000	89.21	0.8921	1120.95
	1500	95.46	0.9546	1571.34
	2000	96.86	0.9686	2064.84
	2500	97.74	0.9774	2557.81
288 hours	500	92.02	0.9202	543.36
	1000	92.91	0.9291	1076.31
	1500	93.09	0.9309	1611.34
	2000	94.14	0.9414	2124.49
	2500	94.77	0.9477	2637.97

Table 4.52 : Inhibition efficiency, degree of surface coverage of corrosion inhibition of mild steel in 0.5 M H_2SO_4 at different concentration OG in different periods of immersion.

Periods	Concentration	Inhibition efficiency	Degree of surface coverage(ϴ)	C/ϴ
72 hours	500	79.76	0.7976	626.88
	1000	80.89	0.8089	1236.25
	1500	84.81	0.8481	1768.66
	2000	86.30	0.8630	2317.50
	2500	94.00	0.9400	2659.57
144 hours	500	80.42	0.8042	621.74
	1000	83.34	0.8334	1199.90
	1500	87.03	0.8703	1723.54
	2000	89.76	0.8976	2228.16
	2500	95.47	0.9547	2618.62
216 hours	500	79.46	0.7946	629.25
	1000	83.13	0.8313	1202.93
	1500	86.81	0.8681	1727.29
	2000	89.79	0.8979	2227.42
	2500	90.84	0.9084	2752.09
288 hours	500	79.46	0.7946	629.25
	1000	83.13	0.8313	1202.93
	1500	86.81	0.8681	1727.29
	2000	87.99	0.8799	2272.99
	2500	97.27	0.9727	2570.17

Table 4.53: R^2 values and slopes of the graph of Langmuir adsorption isotherm of the corrosion inhibition of mild steel in 1 M HCl and 0.5 M H_2SO_4 with and without aqueous extract of LH and OG at different immersion time.

Period of Immersion	**LH in 1 M HCl**		**LH in 0.5 M H_2SO_4**		**OG in 1 M HCl**		**OG in 0.5 M H_2SO_4**	
	Slope	R^2 values	Slope	R^2 values	Slope	R^2 values	Slope	R^2 values
72 hours	1.02	0.997	1.012	0.993	1.056	0.999	1.012	0.999
144 hours	1.14	0.9968	1.088	0.956	1.088	0.999	0.950	0.992
216 hours	0.98	0.998	1.207	0.999	0.981	0.996	1.049	0.998
288 hours	1.03	0.9998	1.153	0.980	1.039	0.999	0.8977	0.994

.

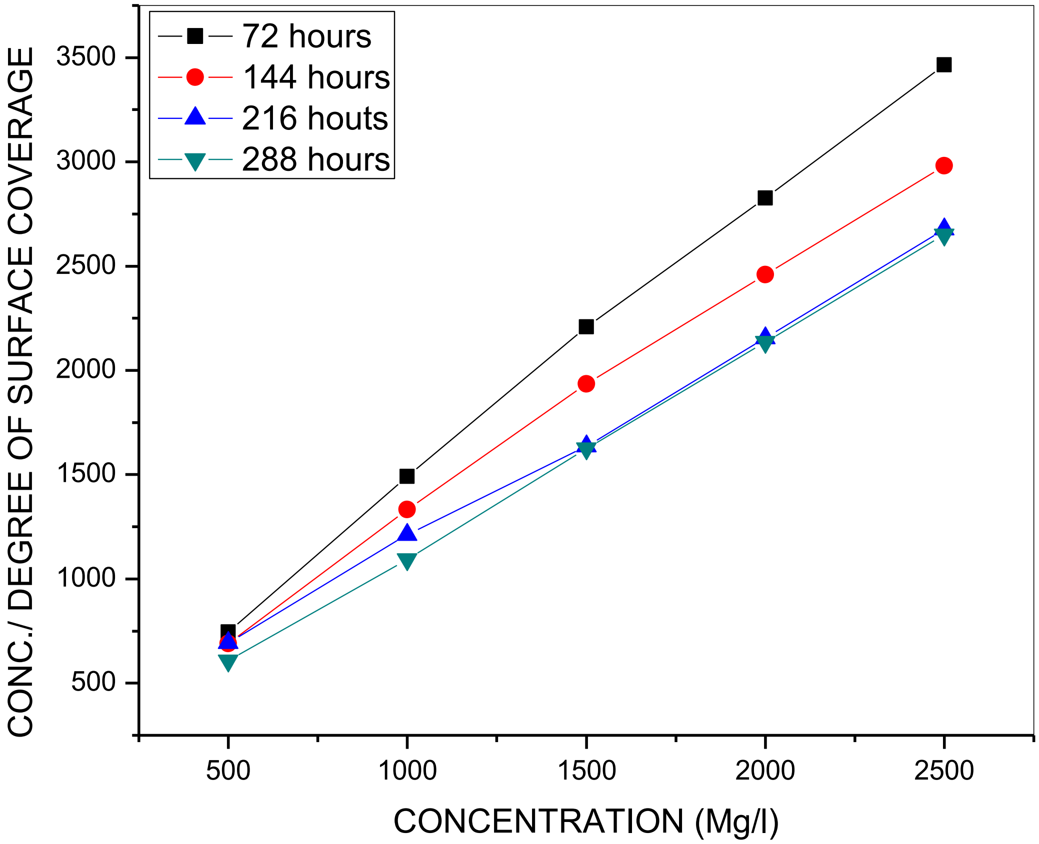

Figure 4.29: Langmuir adsorption isotherm of mild steel corrosion in 1 M HCl in the presence of different concentration of the aqueous extract *Landolphia heudelotii* after 72, 144, 216, 288 hours

Graph obtained is a straight line graph, slopes of the graph are close to unity and values of the linear correlation coefficient R^2 obtained are above 0.95 thus obeys Langmuir adsorption isotherm which implies that the phytoconstituents of LH are adsorbed uniformly on the mild steel surface

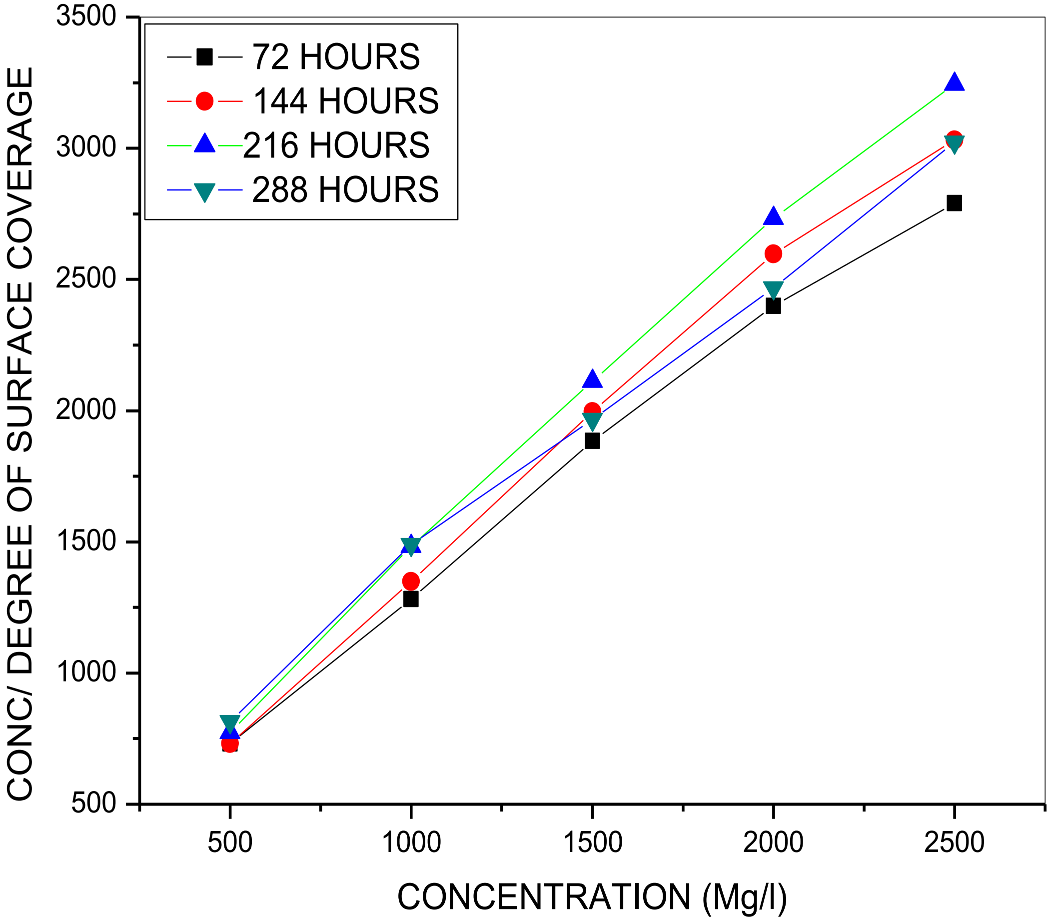

Figure 4.30 : Langmuir adsorption isotherm of mild steel corrosion in 0.5 M H_2SO_4 in the presence of different concentrations of the aqueous extract of *Landolphia heudelotii* after 72, 144, 216 and 288 hours

Graph obtained is a straight line graph, slopes of the graph are close to unity and values of the linear correlation coefficient R^2 obtained are above 0.95 thus obeys Langmuir adsorption isotherm which implies that the phytoconstituents of LH are adsorbed uniformly on the mild steel surface

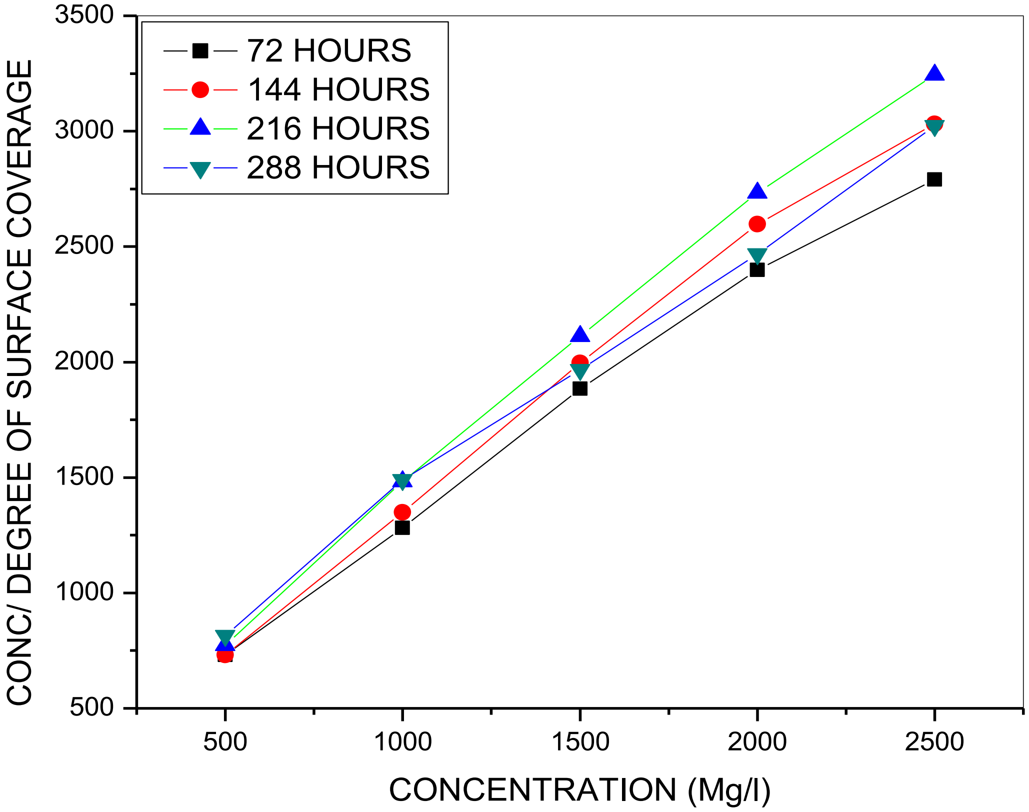

Figure 4.31: Langmuir adsorption isotherm of mild steel corrosion in 1 M HCl in the presence of different concentrations of the aqueous extract of *Ocimum gratissimum* after 72, 144, 216 and 288 hours.

Graph obtained is a straight line graph, slopes of the graph are close to unity and values of the linear correlation coefficient R^2 obtained are above 0.95 thus obeys Langmuir adsorption isotherm which implies that the phytoconstituents of OG are adsorbed uniformly on the mild steel surface

.

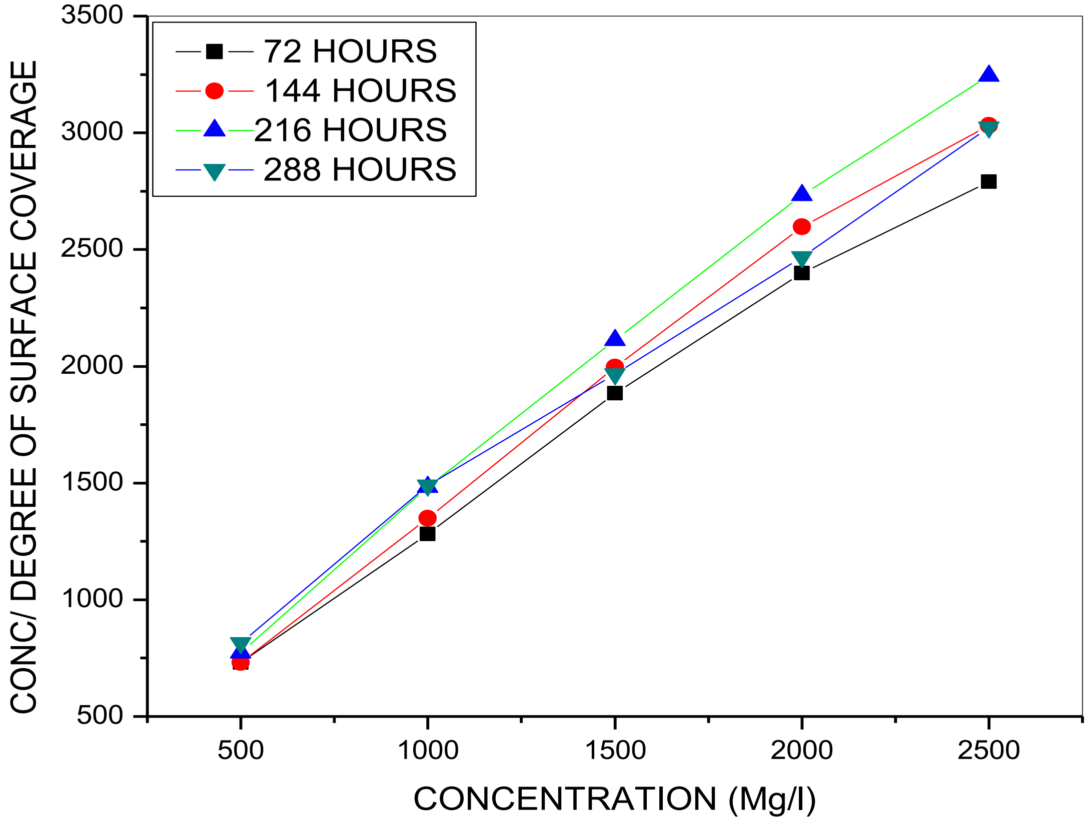

Figure 4.32 : Langmuir adsorption isotherm of mild steel corrosion in 0.5 H_2SO_4 in the presence of different concentration of aqueous extract of *Ocimum gratissimum* after 72, 144, 216 and 288 hours

Graph obtained is a straight line graph, slopes of the graph are close to unity and values of the linear correlation coefficient R^2 obtained are above 0.95 thus obeys Langmuir adsorption isotherm which implies that the phytoconstituents of OG are adsorbed uniformly on the mild steel surface

4.8: Proposed Mechanism of Inhibition

The mechanism of inhibition can be explained based on the mode of adsorption of inhibiting species (i.e whether molecular or ionic), factors such as composition and structure of the inhibitor, the nature of the metal surface, type of acid anion and chemical changes to the extract contributes to the mechanism of inhibition. In addition, structural and electronic parameters such as functional group, steric and electronic effect maybe responsible for inhibition efficiency of any inhibitor. The presence of the phytoconsistuents such as tannins, saponins, terpenoids , flavanoids e.t.c. have been proven from literature to be the major constituents present causing inhibition. These photoconsistuents contains lone pair of electrons present on a hetero-atom (i.e oxygen, phosphorous, sulphur and nitrogen), pi- bond, triple bond (e.g cyano group) in their functional group which are characteristics of a good corrosion inhibitor. They act by blocking the active corrosion sites on the metal surface, thus the adsorption process involves bonding of the free electrons of the inhibitor with the metal. Consequently inhibiting characteristics of the extract can be attributed to the presence of these phytoconsistuents, the main consistuent causing inhibition is beyond the scope of this work because results of analysis does not include isolation of these compounds. Corrosion inhibitors from plant origin are complex in nature therefore it is difficult to isolate the particular constituents that effect inhibition (Hegazy *et al.*,2012; Oguzie *et al.*,2010; Zucchi & Omar,1985). The adsorption mechanism can also be considered from the electrostatic force of attraction existing between inhibiting organic ions and the electrically charged metal surface at the metal/solution interphase. Temperature studies reveals that the inhibition performance of both plant extracts is higher in HCl than H_2SO_4 media. This can be attributed to the nature of inhibitor in both media. A corroding metal specie possesses a positive charge in both HCl and H_2SO_4 media and at such protonated species are poorly adsorbed at the metal/solution interphase (Oguzie, 2006). Also, Cl^- ions in HCl has stronger tendency to be adsorbed on the metal surface hence facilitates physical adsorption of the inhibitor cation than SO_4^{2-} ions . Thus high inhibiting performance of LH and OG in HCl suggests that organic specie present in LH and OG are highly protonated hence are not readily adsorbed on the metal specimen but the high tendency of Cl^- to be adsorbed on the metal surface promotes the adsorption of the inhibitor cation at the metal/solution interphase to form the protective film of insoluble organic complex that protects the metal surface hence explains the high inhibition performance observed in HCl. Results of the energy of activation values indicates that the adsorption process occurred by physisorption and chemisorption but predominantly by physisorption while values of change in Gibb's free energy indicates that adsorption is by physisorption, hence, it can be deduced that the mechanism of the adsorption is mainly by physisorption.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 *Ocimum gratissimum and Landolphia heudelotii* are good corrosion inhibitors of mild steel in 1M HCl and 0.5 M H_2SO_4, gravimetric result reveals highest inhibition efficiency 97.27% and 94.37% in 1 M HCl at 2500 Mg/l; 94.31% and 82.79% in 0.5 M H_2SO_4 at 2500 Mg/l of OG and LH respectively. Temperature studies reveals highest inhibition efficiency of 97.67% and 95 41% in 1 M HCl at 323 K; 94.02% and 93.46% at 313 K in 0.5 M H_2SO_4

Temperature studies which gives an insight to the possible mechanism of the adsorption process suggests physisorption of the inhibiting species in 0.5 M H_2SO_4 at both 500 Mg/l and 2500 Mg/l of OG and LH respectively, activation energy, Ea values was found to be 63.75KJm^{-1} and 65.78 KJm^{-1} in the presence of LH, 102 KJm^{-1} and 68 KJm^{-1} in the presence of OG and 54.76 KJm^{-1} in the absence of both inhibitors, while physisorption mechanism was favoured at 500 Mg/l of both inhibitors, activation energy values was found to be 127.33 KJm^{-1} and 101.51 KJm^{-1} in the presence of LH and OG respectively and 89.37KJm^{-1} in their absence. On the other hand chemisorptions was favoured at 2500 Mg/l of OG and LH in I M HCl respectively, activation energy values was found to be 73.13 KJm^{-1} and 68 KJm^{-1} in LH and OG respectively and 89.37 KJm- ^{1} in their absence, thus the mechanism of the adsorption process is predominantly electrostatic in nature, that is, the organic molecules were physically adsorbed on the corroding metal specimen at the metal/solution interphase. Also, change in Gibb's free energy, ΔG reveals ΔG negative in all cases indicating spontaneity of the process and heat of adsorption Q_{ads} which is approximately equal to AH_{ads} was negative in 0.5 M H_2SO_4 and positive in 1 M HCl which implies an exothermic and endothermic reaction occurring in LH and OG respectively.

Potentiodynamic polarization results shows that the inhibitors are of mixed type, that is both anodic and cathodic reactions are inhibited in the presence of aqueous extract of LH and OG. In addition, values from the graph of adsorption process fits well with Langmuir adsorption isotherm hence the organic species responsible for inhibition were adsorbed on the metal. Results from analysis also revealed that inhibition efficiency maybe as a result protonated nature of the inhibitors, type of acid anion and presence of phytoconsistuents which have been proven to cause corrosion inhibition.

5.2. Recommendation

The study did not extend on the use of electron impedance spectroscopy (EIS) in the study of the corrosion inhibition behavior of the selected plant extracts. EIS has many advantages compared with other electrochemical techniques. It is powerful, rapid, accurate and non destructive method of evaluating the inhibition performance of inhibitors on wide range of materials. It provides detailed information of the system under study and parameters such as corrosion rate, electrochemical mechanism can be investigated. In addition, reaction kinetics and detection of localized corrosion can be determined from experimental data, therefore electron impedance spectroscopy is recommended for further study on this work in other to compare parameters determined from the study, detect any localized corrosion and examine the system under study.

5.3 Contribution to Knowledge

The study has provided an alternative source of corrosion inhibition from plant origin which is safer, economical and eco –friendly in solving the problem of corrosion in our society especially in the industries where metals and alloys are used for various industrial processes involving the use of these acids which facilitates corrosion of these material.

REFERENCES

Abd El – Bouyanzer, Hammounti, A., & Benkaddour, B. (2005). Adsorption preoperties and inhibition of mild steel corrosion in hydrochloric solution. *M.Appl. Surface Science.*, **249**(1), 375 -385.

Abd –El –Nabey, Abdel – Gaber, B. A., Said Ali, A. M., El Khamis, E., & El –Housseiny (2012) .*International Journal of Electerochemical science*. 7 (12), 11811.

Abdallah, M., & Napper, M. M. Ed. (2001) . Cu $^{2+}$ = 3,5 dimethyl pyrazole mixture as a corrosion inhibitor for carbon steel in sulphuric acid solution . *Mater. Chem .Phys* **(71),** 291-298.

Abdel –Garber, A .M ., Abd El-Nabey, B. A., Sidahmed I .M., El- Zayady A .M., & Saadawy, M. (2006). Inhibitive action of some extract on the corrosion of steel in acidic media. Corrosion Science. **48**(9), 2765-2779.

Abdel –Garber, A .M., Abd –El Nabey, B. A., & Saadawy, M.(2009). The role of acidic anion on the inhibition of the extract, corrosion science **5** (5), 1038 -1042.

Abdel –Garber, A. M., Khamis, E., Abo-Eldahab E., & Adeel S. (2008) . Inhibition of Aluminum in alkaline solution using natural compounds. *Material Chemistry and physics* **(109),** 297-305.

Abiola, S., Singh, V. K., & Quaraishi M. A. (2010). Aqueous Extract of Kalmeigh (Andrographi Paniculata) leaves as green inhibitors of mild steel in HCl acid solution. *International Journal of Corrosion*, **212**, 1-10.

Aejiitha, S., Kasthuri, P. K., & Geethamani, P. (2015). Comparision of the corrosion inhibition efficiencies of mild steel in different acidic medium using *Commiphora Caudata* plant extract”. *International Journal of advanced Technology in Engineering and science* **3**(5), 2348-7550.

Agawal, P., & Landolt, D. (1998) . Effect of anions on the efficiency of aromatic carboxylic media. Experimental investigation and theoretical modeling .*Corrosion Science*, **40**(4-5), 673-691 .

Agumen Ham and Gurmeet S. (1991). Pomergrate Alkaloids as corrosion inhibitor for mild steel in acidic medium .*J. Electrchemical Soc*. India , 40(4), 153-157.

Akindahunsi, A. A & Salawu, S. O. (2005). Phytochemical screening nutrient – anti nutrient composition of selected tropical vegetables . *African Journal Biotech.* (**4),** 497-502

Al- Sehabam, H. (2000). Evaluation of extract of Henna Leaves as environmental friendly corrosion inhibitors for metals. *Meter, Wissen Werst Tech.* **31**(12**),** 1060-1063.

Ali, A,. & Folaud, N. (2012). Department of Chemistry, Faculty of science ,Benhal University, Benha Egypt, 45 -76.

Anderson, D. M. W., & Stoddart, J .F. (1996). Studies of Acacia Senegal (gum Arabic) carbohydrate. Res**. (2)**, 104-114.

Arora, P., Kumar, S., Sharma, M. K., & Mathur, S. P. (2007). Corrosion inhibition of Aluminum by capparisdeciduas in acidic medium. *E.Journal of Chemistry*, **4**(4), 450-456.

Ashworth, V. (1996). "Corrosion Management " Proceedings of the 2nd Arabian Corrosion Conference Kuwait, 12-15.

Atkins, P. W. (1998). Physical Chemistry ,Sixth ed., Oxford University Press, 857.

Badui – Dergal Quimica de los Alimentos, Addison Wesley(1999). Longman de Mexico: **45**, 117 -118 ,213,379,396-397.

Bendahou, M., Benabdellah, M., & Hammounti, B. (2006). A study of Rosemary as green corrosion inhibitors for steel in 2 M H_3PO_4. *Pigm Resin Technology* **35**(2), 95 -100.

Benjilali, B., Sarris, J & Richard, H. (1982). Nouveaux Chemotypes and Artemisa herbal science . Aliment **(2),** 515-527

Bjegovic, D., Miksic, B., Stehly, R. (1999). Test protocols for migrating corrosion inhibitors (Mcl) in Reinforced Concrete .Emerging Trends in corrosion control evaluation. Monitoring solutions Vol. 1 , Akademia books. International India Section , New Dehli India, 3 -18.

Bouklah, M., & Hammounti, B. (2006). Thermodynamic Characterization of Steel in Sulphuric acid Solutions by Artemisia, *Port .Electrochemical*, **(24),** 457 – 468.

Bouyanzer, A.M., & Hammounti, B. (2004). A study of anti- corrosion effect of Artemisia oil on steel. *Pigm . Resin Technology* , (**33),** 287 -292.

Buchweishaija, J., & Mhinzi, G. S. (2008). Natural product as a source of environmentally friendly corrosion Inhibitors .The case of natural tree gum exudates from Acacia seyal var seyal, *Portugaliae Electrochemica* **(26),** 257 – 265.

Burkil, A. M. (2004). The useful plant of West Tropical African.Royal botanic gardens Kew, **23**

Chen, G., Zhang, M., Zhao, J., Zhour ., Meng, .Z., & Zhang, Z. (2013). Investigation of Ginkgo biloba leaves extract as corrosion Inhibitors . *Chemistry central*, 7 **(83),** 4-8

Chetouan, I A., Hammounti, B., & Benkaddour, M. (2004). Corrosion inhibition of Iron in Hydrochloric acid Solution by Jojoba oil. *Pigm ,Resin technology* **(33)**, 26 – 31.

Devalapura, R. K., Kamel, M. R., & Arumuga Saamyi P. (1994), Non destructive Technique for corrosion evaluation of steel in concrete. Proceedings of international conference held at the University of Sheffield .(1): 300-309. Concrete Emerging Trends in corrosion control evaluation .Monitoring solutions Vol. 1 ,Akademia.

El –Etre, A. Y. (2008) . *Material Chemistry and Physics*, **(2),** 108 - 163.

EL-Meligi, A. (2010). Corrosion prevention strategies as a crucial need for decreasing environmental pollution and saving Economics. *Corrosion Science* ,**(2),** 22-23

Elsener, B., & Wojtas, H., & Bohni, H. 24 -28 July,(1994) Galvonostatic pulse measurement .Rapid on site corrosion monitoring proceedings of international Conference held at the University of Sherfield **(1)**, 236-246.

Elsevier (1975). Adsorption on heterogeneous surfaces, the exponential Equation for overall adsorption isotherm. *Jaroniec surface science*: 45-50.

Eltre, A. Y. (2007). Inhibition of acid corrosion of carbon Steel using aqueous extract of Olive leaves. *Journal of colloid and interphase science,* **314**(2), 578-583.

Farooqi, H. I., Quraishi, M. A., & Saini, P. A. (1997). Natural products as corrosion inhibitors for mild steel in industrial cooling system. Proceedings from European Federation of Corrosion (EUROCORR '97) Vol.1, Trondheim Sept. 22-25, 186-194

Fountana, M. G., & Greene, N. D. (1967). Corrosion Engineering, McgGraw–Hill Book Cooperation New York, 70 -95

Glew, R. H., Vanderjagt, D. J ., Lockett, C., Grivetti., Smith, L. E., Pastuszyn, J. C., & Millson, M. (1997). Amino acid, fatty acid .*International Journal of food science and nutrition,* **(44),** 1-16.

Hackerman, N., & Snalely E. S. (1984). Corrosion Basics , L.S.V. Delinder (ed) ,NACE Houston , Texas., 78-90.

Hotlets, F. B., Ueda – Nakamura, T., Cortez, D. A .G., Margado- Diaz, J. A., & Makamura, C. V. (2003). Effect of essential oils of Ocimum gratissimum on trypanosomatid Herpetomonas Samuel Pesioa. *Journal of colloid and interphase science,* **12**(4), 45-55.

Hu, Cang, Zhenghao, Pa, Jinling, Shao & Wenyan, Shi, Qi, Xu. (2013) " Corrosion Inhibition of mild steel by Aloes extract in HCl solution medium. *Journal of Electrochemical Science*, **8** (2013), 720-734

Hubert, G., Elmar–Manfred, H., Hatrmut, S. (2002). "Corrosion Ullmann's Encyclopedia of Industrial Chemistry ,Wiley – VCH : Weinhem . Ishtiaque .A., Rajendra .P., & Quarashi, A. M. (2010) . Inhibition of mild steel in acidic solution by Phenramme drug. Experimental and theoretical study. *Corros Sci*.(52), 3033 – 3041.

James, A. O & Akaranta, O. (2009). The inhibition of corrosion of Zinc in 2M hydrochloric acid solution with acetone extract of red onion skin. *Afri. Journal .Pure Appl. Chem.* 3**(11),** 212-217.

JECFA/ FAO (1990). Specifications for identity and purity of certain food additive, Food and nutrition FAO Rome, p 49.

Jones, D. A. (1996) . *Corrosion principles and prevention of corrosion,* (2nd Edition, pp. 354-401) United Kingdom: Pretnice Hall.

Kiliskic, M. Radosevic, J., Gudic, S., Katalinic, V. (2000). Aqueous extract of Rosemarinus alloy corrosion in chloride solution . *Journal Appl. Electrochem.* **30**(7), 823-830.

Kone, W. M. K., Kamanzi, Atindehou (2008). Ethanobotanical inventory of Medicinal Plants used in Traditional veterinary medicine in North Coted'voire (West Africa). *South African Journal of Botany* **4** (74)**,** 76-84.

Kumar, S., Araora, S., Sharma, M., Arora & Mathur (2009). Synergistic effect of Calotropis plant in controlling corrosion of mild steel in basic solution . J. Chili. *Chemical Soc.* 54**(1**), 83-88.

Kumaravel, M., Ramashkumar, S., Subremanion, J. S., Gown, S., Rajasekara, N., & Selavay, A. (2011). Electrochemical Characterization of the positive film by the unsymmetrical Schiff's base on mild steel surface in acid media. *.Electrochem.*, **561**, 3851-3863.

Labriti, B., Dkhireihe, N., Touri, R., Touhami, M., Sfaira, M., El – Hallaoui, Hammounti, A. , Alami, B. A. (2012) . Syngerism in mild steelsion and scale inhibition by New oxazoline in synethetic cooling water . *Arabian Journal for science and engineering*, **37** (5), 1293-1303.

Lebe A. Nnanna, Israel O. Owate,Emeka E. Oguzie (2014).Inhibition of mild steel corrosion in HCl solution by Pentaclethra macrophylla Bentham extract. *Journal of materials and Engineering.* **4**(5), 171-179

Lebrini, M. E., Robert, A., Lecante & Roos (2011) , Corrosion inhibition of C38 steel in 1M HCL acid medium alkaloids extract from Oxandra asbeckii plant , *Corrosion Science*, **53** (2), 687-695.

Lemoine, L., Wenger, F., Galland, J. (1990). Study of corrosion of concrete reinforcement by electrochemical impendance measurement: Corrosion rate of steel in concrete ASTM STP 1065,N.S.Berke , V.Chaker and D. Whitings., Eds., *American Society for Testing and material* Philadelphia, 118-133.

Levy, A. V. (2002) The corrosion control behavior of protective coatings Technology, *Corrosion science*, **36** (1-2), 387-406.

Liang, .C., Wang , P., Wuan, B., & Hauang, N. (2011). A metal – free Amination of Benzoxazoles *Mater. Corros.* (**62),** 53 -60.

Marcel Dekker (1989). Corrosion protection Handbook 2nd edition ., Schweitzer P.A., Ed. Mansfield F. J. (1973), "Simultaneous Determination of instaneous corrosion rate and Tafel slopes of Polarization resistance measurement *Electrchem. Soc,* 120, 515.

Marcus, P., Maurice, V., Strehbvw, H. H. (2008). Localized corrosion (pitting) : A model of passivity breakdown including role of the oxide nanostructure. *Corrosion science* , **50**(9), 2698-2704.

Minhaji, A., Saina, P. A., Quaraishi, M. A., & Faraoqi , I. H. (1999). Study of Natural product as corrosion inhibitors for industrial cooling systems. Corrosion Prevention and Control 46**(2),** 32-38.

Morris, P. E., &. Scarberry R. C. (1972) . Predicting corrosion rate with potentiostat , *Corrosion Sci.* ,28 (**12),** 44 .

Mukherjere, D., Berchman, J ., Rajsekkar, A., Sundamuthus, S., Thiruchalvam, T & Karaikudi, D. (1997). Plant based alkaloids inhibit corrosion of marine alloys. Anti. corrosion method material . 44 **(3),** 186-194.

Mutasingwa, J. (2004). An assessment of cashew nut liquid as a corrosion inhibitor of mild steel alloys in flowing aqueous system. (M.Sc Thesis , University of Dares Salaam) .lndia

Negm, N. A., Kandile, N. G., Badr E. A., Mohammed, M. A., November,(1994), *Corrosion science* **65** (2012) ,94 – 103.NASA , NASA – TM – 584C, Corrosion control and treatment manual. try , (**5),** 8.

Niketan Patel, Anamika Rawat, Smita Javaham and Girish Menta (2010). Inhibitive action of Bridelia Retusa leaves extract on Corrosion of mild steel in acidic media European Journal of Chemistry .journal home page www.eurichem.com.

Noor, E. A. (2007). "Temperature Effect on the corrosion of mild steel in acidic solution by aqueous extract of Fenugreek leaves "*International Journal of Electrochemical Science,*. (2), 996 -1017.

Odiongenyi, A. O., Odoememelam, S. A., & Eddy, V. O.(2009). " Corrosion Inhibition and adsorption properties of ethanol extract of Vernonia amygalina for the corrosion of mild steel in H_2SO_4. *Portugaliae Electrochemical* , **27(1),** 33-45.

Oguzie, E. E. (2006) . Studies on the inhibitive effect of Ocimum viridis extract on acid corrosion of mild Steel . *Materials chemistry and Physics* 99 **(2-3)**, 441-446.

Oguzie, E ..E., Onuoha, G. N., Ejike E. N.(2007). Effect of Gongrenema latifolum extract on Aluminium corrosion in acidic and Alkaline media. *Pigment and Resin Technology* **(36)**, 44 - 49

Oguzie, E. E., (2008). Corrosion inhibitive effect and adsorption behavior of Hibiscus sabdariffa extract on mild steel in acidic media . *Portuliae Electrochemica* (26), 303-314.

Okafor, P. O., Ikpi, M. E., Uwah, I. E., Ebenso, E. E., Ekpe, U. J., Umoren, S. A. (2008) . Inhibitory action of Phyllantus Amarus extract on the corrosion of mild steel in acidic media. *Corros.SCi.* , **50(**8)**,** 2310 -2317.

Olasehinde, E. F., Olusegun, S. J., Adesina, A. S., Omogbehiri, S. A., Momoh –Yahayah, H. (2010). Inhibitory action of Nicotaiana tobaccumextract in the corrosion of mild steel in HCL. *Pacific Journal of Science and Technology* , **11** (2), 455 -462.

Olusegun, S. J., Adeiza, B. A., Ikeke, K. I., Bodunrin, M. O. (2013) . Jastropha curas leaves as corrosion Inhibitors of mild steel in 1M HCL acid. *Journal of emerging Trends in Engineering and Applied science ;* 4**(1)**, 138-143.

Omogbehin, A. S., Momoh, S. A., & Yahaya H. (2010). Inhibitory action of Nicotiana tobacum extract in the corrosion of mild steel in HCL . *Pacific Journal of science and Technology*, 11**(2**), 455-462

Omotosho, O. A., Ajayi , O. O., Ajanaku, K. O., Ifepe, V. O. (2012) .Environment induced failure of mild steel 2M H2SO4 using Chromolaena Odorata . *Journal of material Enviromental Science* **3***(1*), 66-75.

Pessoa, L.M.,& Luciano, S. M.(2002). Antihelminthic activity of essential oils of *Ocimum gratissimum* and Eugonol activity against Haemoachus contortus vet. Parasitol (**109)**, 59-63.

Philip, J. N. Y., Buchweishaija, J., & Mkayula, L. L. (2002). Mechananistic studies of carbon steel corrosion Inbibition by Cashew nut liquid ,*Tranz ,J. Sci.* **28(**2), 105-116

Puckonus, R. R. (1978) " Controlling corrosive microorganism in cooling water system. Chem .Eng .Ict, 7.

Quraishi, M. A. (2004). The naturally occurring products as corrosion inhibitors Corrosion, 04411.

Raja, P. B., & Sethuraman, M. G (2009). Inhibition corrosion of mild steel in sulphuric acid medium by Calotropis procera .J. P*igment Resin Technology*, **38**(1), 33 – 37.

Raja, K., Rajendra, S., Saanya, R. (2011). Allum sativum (Garlic) extract as non toxic corrosion inhibitors. *Journal of Chemistry* **(2013),** 1 – 4.

Riggs, O. Z. (1973). Theoretical Aspect of corrosion inhibitors by C.C. Nathan (ed) NACE, 233-245

Saedah, R., Al Mhyawi(2014).Inhibitionof mild steel corrosion using using Juniperus plant as green inhibitor. *African Journal of pure and applied chemistry* .**8**(1), 9-22

Saleh, R. M., Ismail, A. A., & El Hosany, A. A. (1982). Corrosion inhibition by naturally occurring substances .The effect of some leaves and fruit peels on the corrosion of steel, aluminium, Znic and copper in acid . *Br. corros. J.* **17**(3) , 131-135.

Salensky, G. (1987). Organic Corrosion Inhibitors. Handbook of coatings Additives, 340 – 356, **(2)**, 681 -688.

Sanghvi, M. J., Shukla, S. K., Misra, A. N., Palh, M. R., & Mehta V. G. N. (2010) , Inhibition of HCL acid corrosion of mild steel by the aid of *Embilica officianalis* terminalia beddirica and Terminalia chebula. (**29),** 7-10

Sankarasam, (2008). Electrochemical Polarization Technique for Corrosion monitoring . *Woodhead Publishing series in metals and surface Engineering*. (1), 49-58..

Saratha, R., & Vasuaha, V. G., (2009). Inhibition of mild steel corrosion in 1 M H_2SO_4 medium by acid extract of Nyctanthes arbortristis leaves , *E.J. chem*. **6**(4)**,** 1003-1008.

Saratha, R., & Meenakshi, R. (2010) ,” Corrosion inhibitor . A plant extract “der Pharma Chemica (**2)** 287 – 294 .

Sastri, V. S. (1998). Green corrosion inhibitors , Theory and practice , Wiley and sons Hoboken NJ. Satapathy A .K., Gunasekaran, G., Sahoo, S. C., Kumar, P. V., & Rodrigues(2009). *Corrosion Science* (**51**) 2848.

Sastri, V. S. (1998). *Corrosion inhibitors . Principles and application.*John Wiley and sons , New York.

Scully, J. C. (1997). Corrosion inhibition of carbon steel in HCL solution by fruit peel aqueous extract. *Bulletin of Electrochemistry*, **13**(8-9), 358- 361.

Shyamala, M., & Kasthuri P. K. (2010). Comparative study of the inhibitory effect of the extract of Ocimum Sanctum, Aegle marmelos and Solanum trilobatum on corrosion of mild steel in HCl medium ,"*International Journal of Electrochemical,* **5**(11), 1698-1712.

Sieradzki, K., Newman, R. C.(1987). Stress –corrosion cracking .*Journal of Physics and Chemistry of solids* . 48(**11),** 1101 – 1113.

Singh, A ., Ebenso, E. E ., & Qurashi, M. A. (2012). Corrosion Inhibition of Carbon steel in HCL solution by Some plant extract. *International Journal of corrosion*, (2012), 1 – 20.

Song, G., Johannesson, B., Hapugoda, S., St. John D. (2004). Galvanic corrosion of Magnessium alloy AZ91D in Contact with an aluminum alloy , steel and Zinc. .*Corrosion Science* **46**(4) : 955-977.

Speller, F. N. (1951). *Corrosion ,causes and preventon.* McGraw –Hill Book Co., New York .

Srivastava, K., & Srivastava, P. (1981). Studies on Plant materials as corrosion inhibitors . *Br.Corros. J* 1 (**4)**, 221-223.

Stern M. and Geary A. L. (1957) , " Electrochemical polarization ,I.A, Theoritical analysis of shapes of polarization curves .*Electrochem. Soc.*, 104: 33-63

Tao, Z., Zhang, S., Li W., Ba, Hov , (2010). Ind. Eng. Chem. Res. (**49**) : 2593 -2599

Thilagavathy, S., Saratha, R (2015). "Mirablis Jalapa flowers extract as corrosion inhibitorsof mild steel corrosion in 1M HCl. .*Journal of applied Chemistry* **8**(1), 30-35

Umeron, S. A ., Obot, I. B ., Ebenso, E. E., Okafor, P. C., Ogbebe O., & Oguzie, E. E. (2006). Gum Arabicas potential Corrosion inhibitor for Aluminum in alkaline medium and its adsorption characteristics. *Anti Corrosion methods and Materials,* **53**(5), 277-282

Umoren, S. A., Eduok, U. M., & Oguzie, E. E. (2008). Corrosion inhibition of mild steel in 1M H2SO4 by Polyvinyl pyrrolidone and Synergistic iodide additive . *Portugaliae Electrochemica,* 6(**6)**, 533-546.

Umoren, S. A., Ogbobe, I., Ebenso E. E., & Ekpe, U. J. (2000). Effect of Halide ions on the corrosion Inhibition of mild steel in acidic medium using Polyvinyl alcohol. *Pigment and Resin Technology* 35(**5)**, 284-292.

Umoren, S. A., & Ekanem, U. F. (2010). Inhibition of mild steel in H_2SO_4 using Exudate gum from Pachylobus Edulis and synergistic potassium Halides additives. *Chemical engineering communication* . 197 (**10),** 1339 -1356.

Unlig, H. H., Tradis, D. N., & Stern, M., Feb. (1955). "Corrosion inhibition of Iron by Polyphosphates," *Electrochemical Society* , .597.

Uwah, I. E, Ugi, B. U., Ikeuba, A. I., & Etuk, K. E (2013) ," Evaluation of inhibitive action of eco – friendly Benign costus afer stem extract on the corrosion of mild steel in 5M HCL. *International Journal of Development and sustainability* , 2.**(3)**, 1970 -1981.

Vasant, P. C., & Bansal, G. K. (2013). An investigation into the environmental impact of Atmospheric corrosion of Building materials. *International Journal of chemical sciences and application* 4(**1)**, 1 – 6.

APPENDIX 1

SOLVENT EXTRACTION OF *OCIMUM GRATISSIMUM* AND *LANDOLPHIA HEUDELOTII*

OCIMUM GRATISSIUM

Weight of ground leaves	40g
Weight of handkerchief	11.4092
Weight of handkerchief and residue	29.9504

Weight of ground leaves	40g
Weight of residue	31.4582g
Stock concentration	8.5412g
Initial volume of Solvent (water)	2000ml
Finial volume of water	1950ml
Concentration of extract	$\frac{\text{mass of stock}}{\text{Remaining vol. of water}} \times 1000$
	$\frac{8.5412 \times 1000}{1950}$
	4.495g/l
Converting to mg/l	4.495g/l × 1000
	4495mg/l

APPENDIX II

PREPARATION OF VARIOUS CONCENTRATION OF *OCIMUM GRATISSIMUM* (OG): 500mg/l, 1000mg/l, 1000mg/l, 1500mg/l, 2000mg/l, 2500mg/l

Applying dilution formular $C_1V_1 = C_2V_2$

Where C_1	Stock concentration
V_1	Unknown volume
C_2	Finial concentration
V_2	Known volume

Subsistuting to obtain volume in ml

500mg/l	33.37ml
1000mg/l	66.74ml
1500mg/l	100ml
2000mg/l	133.48ml
2500mg/l	166.48ml

LANDOLPHIA HEUDELOTII (LH)

Weight of biomass	40g
Weight of handkerchief	10.21g
Weight of residue and handkerchief	30.95g
Stock concentration	9.05g
Initial volume of water	2000ml
Finial volume of water	1900ml
Concentration of extract	$\frac{\text{mass of stock}}{\text{Remaining vol. of water}} \times 1000$ $\frac{9.05 \times 1000}{1900}$ 4.7632

Converting to mg/l 4.7632 ×1000

4763.16mg/l

Applying the dilution formula stated above to obtain the volume in ml for the concentrations of 500mg/l, 1000mg/l, 1500mg/l, 2000mg/l and 2500mg/l

500mg/l	31.5ml
1000mg/l	62.98ml
1500mg/l	94.5ml
2000mg/l	125.97ml
2500mg/l	157.46ml

APPENDIX III

PREPARATION OF 0.5 M H_2SO_4 AND 1 M HCl

1 M HCl and 0.5 M H_2SO_4 were prepared using the mathematical expression stated as follows;

$$V_c = \frac{CD\ VD\ Mm}{10 \times PS}$$

Where Vc = Volume of the of the concentrated H_2SO_4 and HCl to be diluted.

C_D = Molar concentration of the acid to be used (ie 0.5 M H_2SO_4 and 1 M HCl)

V_D = Volume to which dilution is to be made.

P = % composition of the concentrated acid

S = Specific gravity of the concentrated acid.

M_m = Molar mass of the acid to be used.

APPENDIX IV

CALCULATION OF THE AREA OF COUPON USED

The parameter of the coupons was calculated as follows :

Length of coupon	30cm by 30cm
Width of coupon	30cm by 30cm
Thickness	0.5mm → 0.005dm
Diameter	2mm → 0.02dm
Radius of coupon	1mm → 0.01dm
i.e 100mm	1dm
Area of coupon	$2LW + 4tL - 2\prod rL$
Where L	Length of coupon
W	width of coupon
t	thickness of coupon
r	radius of coupon

APPENDIX V

CALCULATION OF CORROSION RATE AND INHIBITION EFFICIENCY FROM GRAVIMETRIC STUDIES

Corrosion rate $= \dfrac{\text{Weight loss } (\Delta W)}{\text{Area} \times \text{Time}}$

C R $\dfrac{\Delta W}{AT}$

ΔW Weight loss(g)

A Area of coupon(cm^2)

T Time in hour

Inhibition efficiency (I.E) $= 1 - \dfrac{W_{inh}}{W_{blk}} \times 100$

Where W_{inh} = weight loss in inhibitor

W_{blk} = weight loss in blank

APPENDIX VI

TEMPTRATURE STUDIES

CALCULATION OF ACTVATION ENERGY

$$\ln \frac{CR2}{CR1} = \frac{Ea}{R}\left(\frac{1}{T1} - \frac{1}{T2}\right)$$

where CR_1 and CR_2 are corrosion rates at T_1 and T_2 respectively, Ea is the activation energy of reaction and R is the rate constant.

CALCULATION OF GIBB'S FREE ENERGY

Gibb's free energy of reaction was also calculated by using the expression

$$\Delta G = -2.303\ RT\ \mathrm{Log}\ (55.5K_{ads}.)$$

Where K_{ads} the adsorption constant is expressed as follows : $K_{ads} = \frac{\theta}{Cinh\ (1-\theta)}$

Where θ is the degree of surface coverage obtained from Langmuir adsorption isotherm, c_{inh} is the various concentrations of the inhibitors , T is the temperature and R is the rate constant

HEAT OF ADSORPTION OR ENTHALPY OF ADSORPTION.

The heat of adsorption which is approximately equal to enthalpy of adsorption is calculated using the expression below

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta}{1-\theta_2}\right) - \log\left(\frac{\theta}{1-\theta_1}\right)\right] \times \frac{T_1 T_2}{T_2 - T_1}$$

Where θ_1 and θ_2 are the degree of surface coverage at temperature T_1 and T_2 and R is the rate constant.

APPENDIX VII

ELECTROCHEMICAL STUDIES.

From Potentiodynamic Polarization

$$\text{Inhibition Efficiency (\%)} = \frac{I_{corr}(blank) - I_{corr}(Inh)}{I_{Corr}(blank)}$$

Where

$I_{corr}(blank)$ = corrosion current without inhibitor

$I_{Corr}(inh)$ = corrosion current with inhibitor.