POTENTIALS OF EXTRACTS OF AFRICAN STAR APPLE AND COCK'S COMB LEAVES AS CORROSION INHIBITORS FORMEDIUM CARBON LOW ALLOY STEEL IN ACIDIC MEDIA

BY

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APRIL, 2016

DECLARATION

I declare that the Dissertation entitledPotentials of Extracts of African Star Apple *(Chrysophyllum albidium))* and Cock's Comb *(Heliotropium indicum)* Leaves as Corrosion Inhibitors forMedium Carbon Low Alloy Steel in Acidic Mediawas carried by me in the Department of Mechanical (Production Option) Engineering,under the supervision of Engr. (Prof.) S. A. Yaro and Engr. (Prof.) D. S Yawas, Faculty of Engineering, Ahmadu Bello University, Zaria, Nigeria.

The information derived from the literature is duly acknowledged and a list of references provided. No part of this dissertation was previously presented for the award of a degree at this or any other Institution.

Malomo O. E.		**5st of April, 2016**
Name	Signature	Date

CERTIFICATION

This Dissertation entitled "**Potentials of Extracts of African Star Apple *(Chrysophyllum albidium))* and Cock's Comb *(Heliotropium indicum)* as Corrosion Inhibitors for Medium Carbon Low Alloy Steel in Acidic Media"**by Malomo Olasupo Ebenezer (P13EGME8068) meets the regulations governing the award of the degree of Master of Science in Mechanical Engineering of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This dissertation is dedicated to the memory of my motherlate MrsSilifat Malomo (Nee Agbaje) and mybossom friend Samson Oladipo Egbedeyi (of blessed memory).It is painful that they are not alive to witness this day despite their desires, prayers and pieces of advice.

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ABSTRACT

The potentials of African Star Apple *(Chrysophyllum albidium;* (CA) and Cock's Comb *(Heliotropium indicum;*(HI)as corrosion inhibitorsfor medium carbon low alloy steel in 1.0M H_2SO_4 and HCl acidic media were evaluated and compared with a known conventional standard inhibitor (*Shell Ensis SX;* (SE)).The plant extracts were first characterized to determine their phytochemical constituents; saponins, tannins, alkaloids and flavonoids. These constituents were found to be present. Proximate analysis and physicochemical parameters such as pH, colour, viscosity and solubility of the extracts were also evaluated. The rheological and biodegradability of plant extracts were studied, *Chrysophyllum indicum* showed a shear-thickening behaviour while *Heliotropium indicum* gave a shear-thinning behaviour, rapid biodegradation occurs in the formulated plant extracts during Organization for Economic, Cooperation and Development (OECD) marine Biochemical Oxygen Demand (BOD) tests. Ultraviolent-visible (UV-Vis) and Fourier Transform Infra-Red (FTIR) spectrometry were used to characterize the bioactive compounds present in the leave extracts. Corrosion inhibition efficiencies and ability of the plant extracts were studied by weight loss and Linear Resistance Polarization (LPR) techniques. Solutions of concentrations ranging from 100 to 500part(s) per million(ppm) of formulated and standard inhibitors were prepared. Results showedthat inhibitionefficiencies (IE %) increasedwith increase in concentration of inhibitors for gravimetric-based mass loss and electrochemical methods. For gravimetric based mass loss studies, rate of corrosion decreased progressively with increase in inhibitor concentration and exposure time. Potentiodynamic polarization curves revealed that the studied inhibitors function as mixed–type inhibitors withinhibition efficiency values of 98 % (CA) and 96% (HI and SE) respectively at concentration of 500ppm of inhibitors. Kinectic and thermodynamic studies showedthat inhibitionmechanism occurs due to the adsorption of the inhibitor molecules onto the steel surface is an endothermic process; both physical and chemical takes place on metal surface and best described by the Langmuir isotherm. Scanning Electron Microscope (SEM) analysis after corrosion test showed the appearance of smooth surfaces for inhibited solutions, which may be due to the absorption of inhibitor molecules onto the metal surface that serves as a protective layer. Mechanical properties decreased drastically for uninhibited samples but increased with application of inhibitors.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of Study

Steel of different grades are extensively used in numerous applications, such as oil and gas pipelines, offshore structures, and industrial equipment (Lebrini*et al.*, 2011). Also, they find extensive use for storage tanks and farm machinery system in whichthey are expected to provide specific desirable combinations of better properties such as strength, toughness, formability, weldability and atmospheric corrosion resistance than carbon steel. Stainless steels may be the best choice but are limited by cost constraints. Cost considerations may lead to pruning down to other acceptable material types with built-in safety net with regards to having plans for maintenance (repair or replacement).

Corrosion causes gradual decay and deterioration in metals when exposed to the action of fluids in industrial processes.Among the effective methods of combating corrosion, the use of inhibitors is one of the best and widely used methods for steels in the oil and gas industry and has proven to be very successful (Ebenso, 2011).

The safety and environmental issues in the use of corrosion inhibitors have always been of global concern. Safety is an important consideration in selecting any material in order to meet stringent requirements for engineering application among otherproperties such as mechanical, relative weight, reliability, cost and availability. Notwithstanding the importance of theenvironmental impact of corrosion as a problem which has been a motivation over the years for researchers to

focus on the use of corrosion inhibitors from the eco-friendliness, biodegradability and renewability point of view.

More recently, the practice of corrosion inhibition is greatly influenced by legislations developed such as the US Environmental Protection Agency (USEPA, 1996) and Organization for Economic Cooperation and Development (0ECD, 1984; 2004)as a result of chronic hazardous effects of some compounds, especially those that contain hexavalent chromium ions (Revie and Uhlig, 2008; Sangeetha *et al., 2011*). The injection of film-forming corrosion inhibitors is a common practice to protect carbon steel against internal and external corrosion, plant extracts possess potentialsas corrosion inhibitors, thereby the trend in replacing some common hazardous inhibitors with inhibiting action of bio-extracts to form a protective barrier between the steel surface and the corrosive species in the fluids, irrespective of the corrosive environment**(**Sangeetha *et al., 2011;* Amitha*et al.,* 2012).

Most of the inorganic inhibitors are synthetic in nature which pose chemical treat to the environment thereby limiting their usages. Moreover, bio-extract by simple procedure with presence of constituents like tannins, flavonoid, terpenoid, alkanoids and saponins are obtainable from plants extracts, a cost effective, eco-friendly, and biodegradable renewable sources of materials (Yin Jin, 2004; Omotoyinbo*et al*., 2013). The use of plant extract as inhibitors is gaining research trend due to their mode of inhibiting action and economically friendly(Amitha*et al.,* 2012).

Organic compounds containing nitrogen, oxygen, phosphorous and sulphur are the widely used inhibitors (Yaro *et al*., 2010). Corrosion inhibition by organic compounds takes effect generally by mechanism of absorption of molecules and ions at metal surface. Inhibitors retard corrosion

either by physisortion (electrostatic) or chemisortion (charge transfer) depending on their chemical structure and nature. However, the chemical composition and structure of various plant extracts used as inhibitors is another significant factor influencing surface-active principles when exposed under the action of fluids in various service conditions**(**Sangeetha *et al., 2011).*

1.2 Statement of the Research Problem

Studies have that showninhibitors play a vital role in combating metallic corrosion, especially in acidic media but those that are non-toxic or have low toxicity are the widely used ones (Nnanna*et al.,* 2012). One of the main draw backs with most of synthetic type organic inhibitors is their severe environmental hazards such as toxicity, expensive to synthesize, non-biodegradation and bioaccumulation. Hence, these deficiencies have prompted the search for their replacement.

Recently, researches in corrosion control and prevention are concentrated withthe development of "green corrosion inhibitors". These are compounds with good inhibition efficiency and low risk of environmental pollution. Green corrosion inhibitors are biodegradable and do not contain heavy metals or toxic compounds.Green approaches to corrosion mitigation entail the use of naturally occurring compounds in a sustainable way, while protecting the environment (Amitha*et al.,* 2012). Therefore, there is the need to put more efforts.

Most countries in West Africa especially Nigeria are endowed with forests and luxuriant pastures, among which grow many plant origin with potential bioactive properties for green corrosion inhibitors. Plants are available in nature and considered as the most natural of all the other natural things and, therefore attracted the attention of scientific community due to environmental benefits.

Over the years, numerous classes of organic compounds have been investigated as corrosion inhibitors.Chrysophyllum albidium and Heliotropium indicum are one of the most popular plants, their natural occurrence have been reported in diverse zones in Nigeria but has not been maximally utilized.Although, Chrysophyllum albidium (African star apple) is a forest tree widely known for its fleshy pulp of the fruits while the popularity of Heliotropium indicum as a vegetable is due to the distinct, pleasant aroma it releases when used in cooking soups in northern Nigeria. They are known to possess several antioxidative capacities and bioactive compounds (Akaneme, 2008; Jyoti and Sharma, 2014).

*Chrysophyllum albidium*and *Heliotropium indicum*plants are of interest, because of theiravailability,more importantly relatively less expensive andenvironmentally friendlyamidst other plants of biodegradable and renewable sources. Most of the compounds extracted from these plants are been used in traditional medicinal applications such as aromatic spices, medical plants and herbs (malaria therapy and pharmaceutical drug development). However, the use of their extracts as corrosion inhibitors to best of my knowledge has not been tested.

1.3 The Present Research

In spite of great number of bio-extracts assessment as corrosion inhibitors carried out and reported in the literature, researchers have continued to identify more bio-extract as inhibitors for specific applications (Yaro *et al.,* 2010). However, no work so far carried out on*Chrysophyllum albidium*and*Heliotropium indicum* leaves extract using electrochemical studies for low alloy steel inhibition, and coupled with the fact it readily available within the proximity of this research work.Even then, there is need for further research to be done in this direction, notwithstandingthe development of effective corrosion inhibitor which is the trust for this study.

The present research focused on the use of*Chrysophyllum albidium*and*Heliotropium indicum* leaves extract as organic inhibitors for medium carbon low alloy steel in 1M HCl and 1M H_2SO_4environments.

1.4 Aim and Objectives of the Research

The aim of this research is to assess the suitability of utilizing extracts of *Chrysophyllum albidium*and*Heliotropium indicum* leavesas corrosion inhibitors of medium carbon low alloy steel in 1M HCl and 1M H_2SO_4environments.

While the specific objectives of the research are to:

(i) Assess the biodegradability limits of formulated and standard Shell Ensis SX inhibitors using OECD Marine BOD model.

(ii) Carry out corrosion tests on medium carbonlow alloy steel using gravimetric basedmass loss and linear resistance polarization techniques in the presence and absence of the formulated and standard inhibitors.

(iii) Carry out mechanical tests and microstructural examination on the low alloy steel before and after corrosion test.

1.5 Justification for the Research

The problem of corrosion has been a subject of concern for several years and this happens to be one of the major problems facing many industries in the world today; ranging from the petroleum industries to mining industries and even to our everyday life. Several countries and industries all over the world have spent and allocated huge sums of money into researches aimed at combating this menace.

Also, environmental protection has become a major consideration in the petrochemical industry which has led to reduction in the use of inorganic and/or synthetic inhibitor.Asides, the use of agro-based organic corrosion inhibitors to protect structures in services had been reported to have little or no adverse effects on the environment, as well as reduce the rate of corrosion in practice such as the oil well acidizing and offshore drilling operations.

1.6 Scope of the Study

The scope of the work encompasses the followings:

(i) Elemental analysis of as-received steel sample by Emission Optical Spectrometer

(ii) Extraction of compounds from ground *Chrysophyllum albidium*and*Heliotropium indicum* leaves using the Soxhlet extractor.

(iii) Corrosion inhibition tests by gravimetric based mass loss and linear polarization resistance methods.

(iv) Chemical analysis of the formulated inhibitor by Fourier Transform Infrared (FTIR) and Ultraviolent (UV) Spectroscopy.

(v) Biodegradability tests of *Chrysophyllum albidium, Heliotropium indicum* and Shell Ensis *SX* inhibitors by OECD Marine BOD Model for 28 days.

(vi) Scanning Electron Microscope (SEM) analysis of medium carbon low alloy before and after corrosion test.

(vii) Mechanical tests such as hardness, impact and tensile strength of the steel sample before and after the corrosion test.

1.7 Contribution to knowledge

This work has a number of significant contributions to the field of corrosion science and engineering in corrosion control and prevention. Among these contributions have implications for researchers, practitioners and educators.

(1) The primary goal of this research is the development of organic corrosion inhibitors for low alloy steel in acidic environment from the extracts of *Chrysophyllum albidium* and *Heliotropium indicum* leaves. Organic inhibitors were successfully formulated and tested.

(2) Formulated inhibitors from extracts of *Chrysophyllum albidium* and *Heliotropium indicum* leaves has greater tendency of degradation far more than that of Shell Ensis SX inhibitor formulation thereby does not show clearly duration over which it will persist in the environment based on the results obtained from the OECD marine BOD model studies in this research.

(3) Extracts of*Chrysophyllum albidium* and *Heliotropium indicum* leaves will serve as effective and eco-friendly inhibitors for medium carbon low alloy in acidic media with inhibition efficiencies percent upto 98.2 and 96.0 respective, thereby complete favourably with the value of 96.2 obtained for Shell Ensis SX standard inhibitor.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 CORROSION

Corrosion is the degradation of a material caused by environmental interaction (Revie and Uhlig 2008). It is a continuous and costly problem that encompasses both naturally occurring and man-made materials such as metals, plastics, rubber, and aggregates such as concrete, composites materials; and woods.

2.1.1 The Nature of Metallic Corrosion

Corrosion is an electrochemical reaction which is caused by the flow of direct electrical current (d.c.). The electrochemical reaction is destructive in nature caused by the flow of direct electrical current (d.c.), and involves anodic and cathodic reaction. The anode is the part of the metal surface that corrodes - that is, the metal that dissolves in the electrolyte with loss of electrons which is called oxidation (2.1). The oxidation causes the actual metal loss but the reaction, maintaining charge neutrality. Otherwise, a large negative charge would rapidly develop between the metal and the electrolyte and the corrosion process would cease.

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.1)$$

Where 2.1 is the anodic reaction for corrosion of iron in water (Fig. 2.1), Iron ion goes into solution and the two electrons are left behind in the metal.

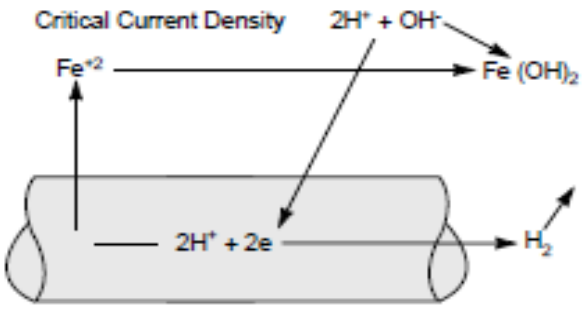


Fig. 2.1: Corrosion of Iron in Water (Sastri*et al.*, 2007)

The cathode is that portion of the metal surface that does not dissolve. It is the site where electrons generated as the iron dissolves at the anode travel through the metal to the cathodic surface area. There are two primary reactions possible at the cathode, the "hydrogen evolution reaction" and the "oxygen absorption reaction." Other reactions are possible but are encountered less often. In the hydrogen evolution reaction, the electrons combine on the surface of the metals with hydrogen ions in the electrolyte to form hydrogen molecules, which escape as gas bubbles (2.1 and 2.3). If, as is usually the case, dissolved oxygen is present in the water, another cathodic reaction can occur, the reduction of oxygen: This consumption of electrons is called a reduction reaction and is as follows:

$$2H^+ + 2e^- \rightarrow H_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.2)$$

$$\tfrac{1}{2}\, O_2 + H_2O + 2e \rightarrow 2OH^- \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.3)$$

As would be expected, increasing the amount of dissolved oxygen increases the corrosion rate of iron. However, at very high dissolved oxygen concentrations, the corrosion rate drops to a very low value. This surprising drop is the advent of the phenomenon called "passivity", a specific form of "polarization".

Passivity is as a result of a thin invisible protective film formed on metal surface either metal oxide, insoluble salt or chemisorbed oxygen, preventing further contact with the electrolyte. In the case of iron, when more oxygen reaches the metal surface than can be used in the cathodic reaction, a protective passive film will be form. A temporary passive iron oxide film is also formed when iron is immersed in concentrated nitric acid. More permanent films are formed on aluminum, titanium and stainless steels and chromium bearing nickel alloys.

In practice, a metal often shows a high initial rate of corrosion. However, in general, the rate often diminishes with time. This effect, known as polarization, might be defined as the change from open-circuit electrode potential as the result of the passage of current. Polarization may result from reactions at either the anode or the cathode. Polarization may result from reactions at either the anode or the cathode.

Anodic polarization – In some corrosion reactions (e.g. iron in aerated water) the corrosion rate diminishes due to an accumulation of insoluble corrosion products which become somewhat protective of the iron anode. This phenomenon, anodic polarization, is defined as the change of the electrode potential in the noble (positive) direction due to current flow. Other examples of anodic polarization are iron or non-alloyed steel exposed to concentrated nitric, sulfuric and phosphoric acids.

Cathodic polarization – Conversely, polarization can result from reactions at the cathode. For example, when iron is immersed in non-aerated neutral water, the absence of dissolved oxygen permits development of an adsorbed film of hydrogen which likewise reduces the corrosion current. This is known as cathodic polarization and is defined as the change in the electrode potential in the active (negative) direction due to current flow.

Specific corrosion inhibitors may work on either the anodic or cathodic sites, their adsorption causing the same decrease of corrosion current. Strong anodic inhibitors (e.g. chromates, nitrites or even an excess of dissolved oxygen in water) result in the type of anodic polarization known as "passivity". When no current flows between anode and cathode areas, the potential difference between them is at a maximum known as the "open-circuit potential".

As soon as current begins to flow, this difference decreases. This decrease in potential is known as polarization. The decrease in anode potential is anodic polarization; in cathode potential, cathodic polarization. The oxidation and reduction reactions are sometimes referred to as half-cell reaction and can occur locally (at the same site on the metal) or can be physically separated. For a current to flow, a complete electrical circuit is required. In a corroding system (Figure 2.2), this circuit is made up of four components:

(1) The anode is the electrode of an electrolytic cell at which oxidation is the principal reaction. Electrons flow away from the anode in the external circuit. It is usually the electrode at which corrosion occurs and metal ions enter solution.

(2) The electrolyte is a conductive liquid through which the current is conveyed by positively charged ions (cations) to the cathode. Negatively charged anions are simultaneously attracted to the anode.

(3) The cathode is the electrode of an electrolytic cell at which reduction is the principal reaction. Electrons flow toward the cathode in the external circuit.

(4) A metallic path is an external circuit to complete the connection between anode and cathode.

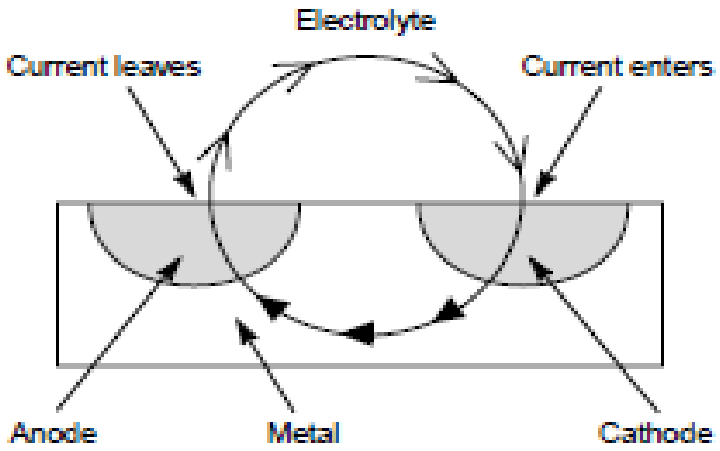


Fig. 2.2: Schematic Diagram of a Differential Corrosion Cell (Sastri*et al.*, 2007)

2.1.2 Parameters Influencing Corrosion Rate

The important parameters influencing corrosion attack can be effectively classified into the material involved and the environment in which it is subjected to. Corrosion attack on the type of material used can be described as follows;

2.1.2.1 Position of Metal in Galvanic Series

It decides the corrosion rate. A metal having higher position in galvanic series undergoes corrosion when connected to another metal below it. Also, more difference in the position of galvanic series will cause faster corrosion at anodic metal.

2.1.2.2 Purity of Metal

Pure metal resists corrosion, while impurities in a metal form a local galvanic cell (metal as anode and impurity as cathode) and result in the corrosion of metal. Corrosion rate increases as a result of exposure of impurities contained in the material. For alloys that have homogeneous solid solution, local action will be impossible, hence no corrosion failure.

2.1.2.3 Relative Areas of Anode and Cathode

Smaller the area of anode compared to cathode will lead to faster corrosion of anode. It is because the corrosion current at anode and at cathode will be same. But for small anodic area the current density will be large at anode and larger cathodic area will demand more electrons which will be fulfilled by fast reaction at anode (oxidation), i.e. rapid corrosion.

2.1.2.4 Physical State of the Metal

Small granular metal will corrode faster than the larger one. Also the type of structure formed by a metal will have effect on the corrosion rate. A bent metal (stress) is rapidly corroded due to stress.

2.1.2.5 Nature of Oxide Film

An oxide film is formed by the reaction between metal and oxygen. If this oxide film is porous and oxygen can be diffused through it, more corrosion is expected. Also, if volume of metal oxide is more than the volume of metal least corrosion or no further corrosion occurs.

2.1.2.6 Atmosphere

Many variables influence the corrosion characteristics of an atmosphere. Diverse factors (e.g. relative humidity, temperature, sulfur dioxide content, hydrogen sulfide content, chloride content, amount of rainfall, dust) and even orientation of the exposed metal, all can effect marked influences in corrosion behavior. The important of environment in the corrosion of a metal cannot be over-emphasized. Environmental parameters like temperature, humidity, pH, etc. play important role. The effect is discussed here.

(1) Temperature: the rate of diffusion increases by rise in temperature; hence the rate of corrosion is also increased. At higher temperature, passive metals also become active and

undergo corrosion. But higher temperature reduces the concentration of oxygen and hence corrosion is reduced.

(2) pH Value: pH value means concentration of H+ (acidic nature). In acidic medium (pH less than 7), corrosion is faster. Also, in basic medium pH > 7, some metals such as Pb, Zn, Al and so on form complexes and hence they corrode. Pourbiax relation between pH of medium and potential of metal deals with the corrosion process and it gives idea how to reduce corrosion (Fig. 2.3).

(3) Humidity: In humidity, gases like CO_2, SO_4, andNO_x are dissolved which form electrolytes. It will cause galvanic corrosion. Some oxides are water soluble, humidity washes away the corrosion products and metal surface is further corroded. Other soluble corrosion products can also be washed away by humidity, causing further corrosion.

(4) Impurity of Atmosphere: Pollutants like H_2S, SO_2, CO_2 and acid vapours cause more pollution where they dissolve. In sea water, salty in nature which acts as an electrolyte, corrosion rate increases. Some suspended particles are dissolved in humidity and form electrolyte which helps in corrosion.

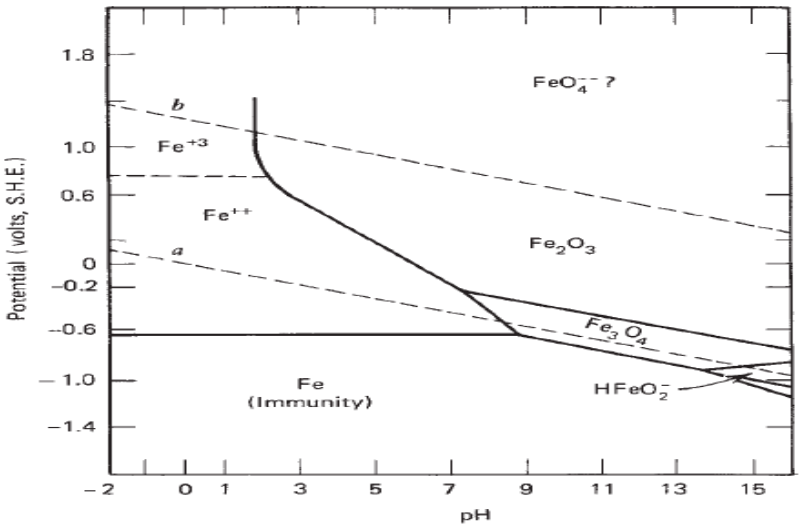


Fig.2.3: Pourbiax diagram of Iron-Water System (Source: Fontana, 1986)

2.1.3 Effects of Corrosion

The consequence for corrosion can causes a great loss of economy and life. The following harmful effects are specific:

(1) Corrosion reduces the thickness of the metal resulting in loss of mechanical strength and failure of the structure.

(2) Corrosion causes structural failure as it is hazardous (e.g. car and aircraft).

(3) Because of the deterioration of appearance, the cost of the machine is reduced.

(4) Efficiency of the machine is reduced due to corrosion.

(5) Because of corrosion, pipes are blocked and pumps are difficult to operate.

2.2 Forms of Corrosion

Corrosion can manifest or take many forms, including general corrosion, galvanic corrosion, crevice corrosion, stress corrosion cracking (SCC), pitting corrosion, intergranular corrosion, parting corrosion, and erosion corrosion and Fontana (1986). They are the major forms of corrosion accounting for the vast majority of corrosion problems observed, along with several lesser seen forms occurring in specific environments. In addition, they are influenced by the corrosive environment, the metallurgical condition of the materials, and the local stresses that are present.

Although, Uniform or general corrosion proceeds independent of the material's microstructure and component design while some forms are localized, dependent upon the environments the components and systems designs, and/or the microstructure of the materials. These forms typically produce higher corrosion rates than uniform corrosion, and in some cases can be quite rapid. They may be classified based on intrinsic and extrinsic modes. Intrinsic modes of

corrosion are mostly independent on design such as general corrosion, stress-corrosion cracking and Intergranular corrosion while extrinsic modes of corrosion are affected by design such as crevice corrosion, erosion corrosion and corrosion fatigue (Sastri*et al.*, 2007). They could be identified based on the apparent morphology of corrosion, using the basic factor influencing the mechanism of corrosion in each form (Table 2.1).

Each of the various forms of corrosion should be evaluated for a material and environment when designing new systems. It is highly dependent upon the service environments and the material's composition, generally occurring at a slow rate (Benjamin *et al.*, 1986).

Also, corrosion can be categorized into several types. The following sections cover basic forms and various sub-categories observed, in relation to their susceptibilities and general protection.

Table 2.1: Morphological Classification of Corrosion (Sastri*et al.*, 2007).

1	General corrosion	Uniform, quasi-uniform, and non-uniform corrosion, Galvanic corrosion
2	Localized corrosion	Pitting corrosion, crevice corrosion, filiform corrosion
3	Metallurgical influenced corrosion	Intergranular corrosion, sensitization, exfoliation, dealloying
4	Microbiological corrosion	Crevice attacks
5	Mechanically assisted corrosion	Wear corrosion, erosion corrosion, corrosion fatigue
6	Environmentally induced cracking	Stress-corrosion cracking, hydrogen damage and embrittlement such as hydrogen-induced cracking, high-temperature hydrogen attack, hot-cracking, hydride formation, liquid metal embrittlement, solid metal-induced Embrittlement

2.2.1 General Corrosion

General corrosion is a uniform attack and is the most commonly encountered type of corrosion. It is characterized by a chemical or electrochemical reaction which proceeds uniformly over the entire exposed surface area. The metal becomes thinner and eventually fails. Uniform corrosion rates are fairly predictable, following an exponential relationship as follows:

$$Corrosion\ Rate\ (C.R) = \frac{K*W}{A*T*D} \quad \text{(eq. 4)}$$

Where K=a constant (derive from table 2)

T=time of exposure, hours (h), to the nearest 0.01 h

A=area, cm2, to the nearest 0.01 cm^2

W= mass loss, g, to the nearest 0.001 g

D=density,$\frac{g}{cm^3}$

Table 2.2: Constant K in corrosion rate equation(NACE, RP0775 2005)

Corrosion Rate Units Desired	**K**
mils per year (mpy)	3.45×10^6
inches per year (ipy)	3.45×10^3
inches per month (ipm)	2.87×10^2
millimeters per year (mm/y)	8.76×10^4
micrometers per year (µm/y)	8.76×10^7

The decrease in corrosion rate with time is a direct result of passivity, which then deters further corrosion from occurring. There are extreme cases however, where the corrosivity of the environment is severe and prevents an oxide layer from forming. In this case, the corrosion rate will be constant with time.

Equation 4 may be used extensively in predicting long-term corrosion damage from short-term tests but often, there are some problems with this prediction however due to the fact that environments usually change over time so that corrosion rates will deviate from those predicted by the equation. Also, the development of additional forms of corrosion will likely accelerate attack in localized areas. Uniform corrosion can be control by:

(1) Slow down or stop the movement of electrons
(2) Slow down or stop oxygen from reaching the surface by coating
(3) Prevent the metal from giving up electrons by using a more corrosion resistant metal higher in the electrochemical series. Use a sacrificial coating which gives up its electrons more easily than the metal being protected.

2.2.2 Localized Corrosion

This form of corrosion dependent upon conditions that may exist that cause corrosive attack in a very specific location or under a specific set of conditions. Such attack is normally referred to as localized. This type of corrosion takes several forms pitting, crevice attack, and microbially influenced corrosion (MIC) are all types of localized corrosion.

Pitting – Pitting is a form of very localized attack that results in the formation of holes in the metal (Plate2.1). While the holes formed are generally small they can propagate very quickly

leading to material perforation and failure in a very short period of time. The micro-environment within the pit itself can be autocatalytic making this a particularly dangerous form of attack.

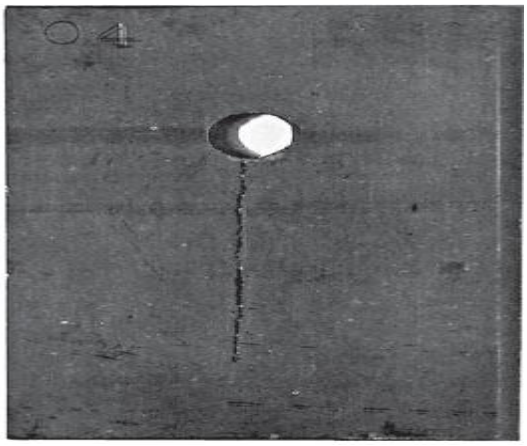


Plate2.1: Diagram of Elongated Pit on Steel Specimen (Source: Fontana, 1986)

Pitting usually grow in the gravitational direction, where cracks may initiate at the edge of a pit due to an increase in the local stress or pits can coalesce underneath the surface, which can weaken the material considerably. Metals owing to their corrosion resistance to their passive state show pitting and ultimately result in formation of passivity. Control can be measured by:

(1) Selecting a resistant material and use of a protective coating

(2) Ensuring a high enough flow velocity of fluids in contact with the material or frequent washing

(3) Control of the chemistry of fluid and use of inhibitors

(4) Maintaining the material's own protective film

Crevice Corrosion – Crevice attack usually takes place in a very tight gap between two surfaces (e.g. as with gaskets or fasteners or under mineral deposits). As with pitting, the micro-environment within the crevice can greatly differ from the general medium. Concentration cells can cause this type of corrosion to progress at a very rapid rate which occurs rapidly in the area with less oxygen. The mechanism of crevice corrosion consists of the oxidation of the metal and

reduction of oxygen, yielding hydroxyl ion. The potential for crevice corrosion can be reduced by:

(1) Avoiding sharp corners and designing out stagnant areas

(2) Use of sealants

(3) Use welds instead of bolts or rivets

(4) Selection of resistant materials

Microbially Influenced Corrosion (MIC) – MIC is a recently identified form of crevice attack. Certain types of bacteria form dome-shaped colonies on the metallic surface. The inside of the structure is sealed from the outside. The life cycle of the bacteria produces a corrosive environment within the colony which causes a crevice attack of the metal. While MIC usually takes place on components exposed to natural water (either fresh or brackish), it has also been encountered in process water in industrial systems. Microbial corrosion can be controlled by:

(1) Selection of resistant materials

(2) Frequent cleaning

(3) Control of chemistry of surrounding media and removal of nutrients

(4) Use of biocides

(5) Cathodic protection.

2.2.3 Environmentally Assisted Cracking

Some types of corrosion take place as a result of chemical conditions within the environment and the mechanical condition of the metal itself. Both conditions must be present for this type of corrosion to take place. Corrosion fatigue, stress corrosion cracking, liquid metal cracking, and hydrogen embrittlement are all forms of environmentally assisted cracking.

Corrosion Fatigue – Corrosion fatigue failure takes place due to the reduction of fatigue resistance of the metal with the presence of a corrosive medium. Thus it is normally encountered not as a visible degradation of the metal but as a premature failure of a component under cyclic conditions. The stress under which the material fails would not normally be considered sufficient to cause failure. This can be reduced or prevented by;

(1) Proper material selection

(2) Good design that reduces stress concentration

(3) Avoiding sudden changes of section

Stress Corrosion Cracking – This refers to the cracking caused by the simultaneous presence of tensile stress and a specific corrosive medium. During this type of cracking, the metal is virtually unattacked over most of the surface while fine cracks progress through at the attack site (Plate 2.2).

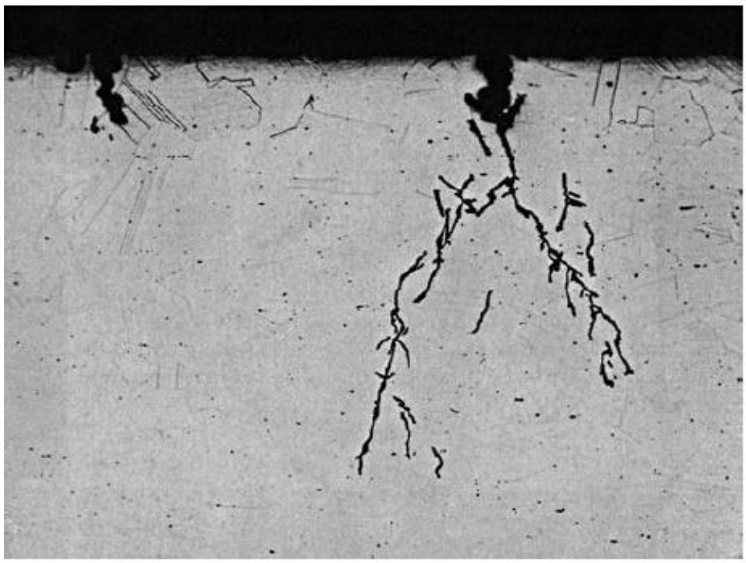


Plate2.2: Diagram of Stress-Corrosion Cracking (Source: Fontana, 1986)

Chloride stress cracking of stainless steels and ammonia stress cracking of nickel-copper alloys are examples of this type of attack. Prevention can be achieved by:

(1) Reducing the overall stress level and designing out stress concentrations

(2) Selection of a suitable material not susceptible to the environment

(3) Design to minimize thermal and residual stresses

(4) Developing compressive stresses in the surface the material

Liquid Metal Cracking – Liquid metal cracking is a specialized form of stress corrosion. The susceptible metal (usually due to residual tensile stresses from fabrication) is attacked (cracked) by a low-melting liquid metal. An example is the cracking of aged Ni-Cr-Fe alloys by silver-base brass alloys.

Hydrogen Embrittlement – Hydrogen embrittlement takes place due to the penetration of the surface of susceptible metals by elemental hydrogen. This can result from the formation of metallic hydride compounds in some materials while in others it takes place by the interaction of dissolved hydrogen atoms. Regardless of the mechanism, the attack results in the formation and propagation of fine cracks and voids in the metallic structure.

Intergranular Corrosion – Intergranular corrosion, as the name implies, is the selective attack of a metallic component at the grain boundaries by a corrosive medium. Several conditions can lead to a material being susceptible to intergranular corrosion. In some environments the grain boundary of a metal simply exhibits the most reactive nature. Because of thermal mechanical processing, metallic compounds may tend to precipitate and migrate to the grain boundaries. If these are more reactive than the metallic matrix, they can be selectively attacked. Metallic reactions can cause areas adjacent to the grain boundary to be depleted of some element, rendering this zone less resistant to attack. A commonly encountered form of intergranular

corrosion is the attack of non-stabilized austenitic stainless steels due to the formation of chromium carbide precipitates and the subsequent depletion of chromium (Fig. 2.4).

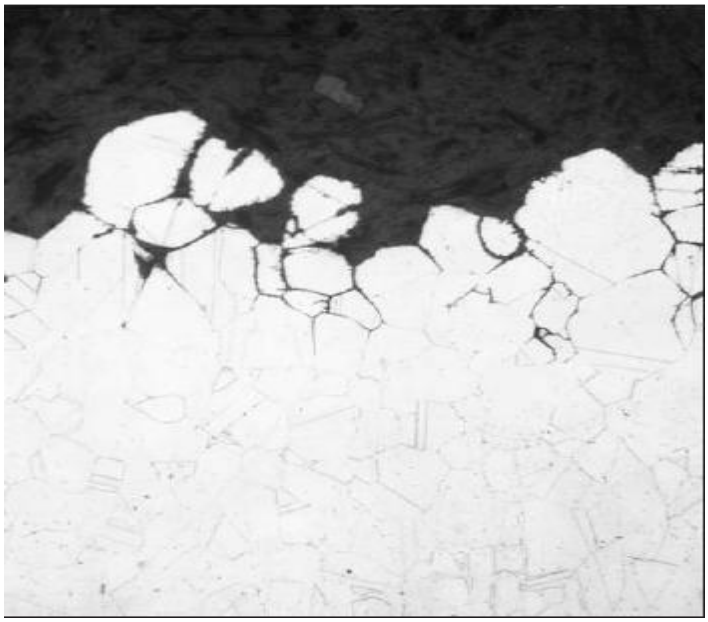


Fig.2.4: Diagram of Intergranular Corrosion (Satri*et. al.*, 2007)

It can be avoided by:

(1) Selection of stabilized materials

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

Erosion Corrosion – Erosion corrosion is the acceleration or increase in rate of deterioration or attack on a metal because of relative movement between a corrosive medium and the metal surface. Generally the movement is rapid and the effects of mechanical wear or abrasion are involved. Metal is removed from the surface as dissolved ions or corrosion products are mechanically swept away from the metal surface. Prevention can be achieved by:

(1) Reducing the flow rate and turbulence

(2) Use of replaceable or robust linings in susceptible areas

(3) Avoiding sudden changes of direction

(4) Streamlining or avoiding obstructions to the flow

Galvanic Corrosion – Galvanic corrosion results from the electrical coupling of two dissimilar metals in a corrosive medium resulting in the attack of the less resistant metal. The metallic differences may be due to metallic structure as well as composition. The less noble material becomes anodic while the more noble becomes cathodic.

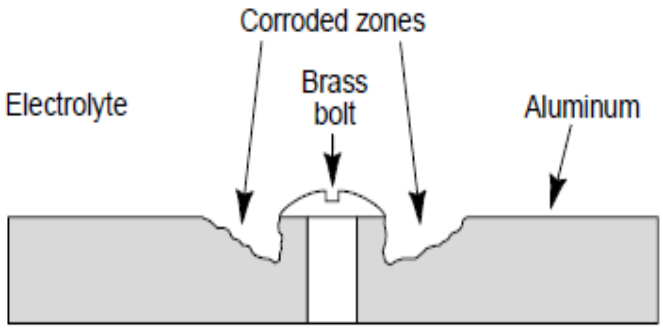


Fig.2.5: Schematic Diagram of Galvanic Corrosion (Sameer, 2013)

Figure2.5 shows the schematic diagram of galvanic corrosion, occurring where the bolt material was more noble than the sheet metal. The anodic material actually protects the cathodic leading to its own accelerated decay. Ranking of materials in an electromotive force (EMF) or galvanic series in a specific media will help determine the propensity of two materials for this type of corrosion. The farther apart the materials are in the series, the greater is the likelihood of attack of the less noble material. Prevention of this problem is based on ensuring that one of the three features does not exist:

(1) Breaking the electrical contact using plastic insulator or coatings between the metals

(2) Select metals close together in the galvanic series

(3) Prevent ion movement by coating the junction with an impermeable material, or ensure environment is dry and liquids cannot be trapped

Dealloying – Dealloying is the selective removal of one element of a solid alloy by a corrosion process. A corrosive medium specifically attacks one component of the alloy. A common example of this type of corrosion is the selective removal of zinc from brass (dezincification).

2.3 Material selection to Ensure Corrosion Resistance

Materials selection refers to the selection and use of corrosion-resistant materials such as stainless steels, plastics, and special alloys to enhance the lifespan of a structure in its intended serviceenvironments. Materials selection personnel must consider the desired lifespan of the structure as well as the environment in which the structure will exist. Materials selection is a crucial part of the design process; however it is a process that can lead to future problems, especially if the designer focuses upon meeting performance requirement while giving little thought to maintenance needs.

The successful consideration of corrosion prevention and control during the materials selection phase of the design process is key to developing systems that will age in a predictable and affordable fashion. It should be noted that the process of materials selection is not used solely to choose the material to build a structure or component. Rather, it is used to select a system of materials that together provide the necessary mechanical, thermal, electrical, and physical properties needed to meet performance requirements while simultaneously providing the necessary resistance to environmental attack including corrosion (**Benjamin *et al.*, 1986).**

2.4 Impact of the Corrosive Environment

Planning for the graceful aging of a structure or system during materials selection requires a firm understanding of the service environments. The word environment used here describes the

conditions a system may be exposed to while in service. For example, the high temperature environment turbine blades experience inside a jet engine during operation. In reality though, things are not quite that simple because systems experience a variety of simultaneous environment conditions.

Systems often contain many fluids and chemicals that are necessary for its components to operate, but some of these can be very corrosive and cause a material to degrade. For instance, designers must consider cleaning chemicals and hydraulic fluids as sources of contamination that can cause a material to corrode (Sastri, *et al.*, 2007). There are many other materials and contaminates that exist within the operation environment that can influence the rate at which a structure or component corrodes. Designers must take a step back and gain a firm understanding of all environmental factors that can influence corrosion before selecting the construction materials. Again, it is important to note that the 'environment' as is described here is not a single condition but rather a combination of factors, which work in concert, such as operating temperature and humidity, salinity, and mechanical loading. Other contributing influences include chemicals, fuel, and pollutants to name a few. Having a firm understanding of the operational environment is crucial to designing a corrosion resistant system.

2.5 The Importance of Corrosion Testing and Information

One of the reasons why the selection of corrosion resistant materials is a challenging process is that corrosion data isn't usually available in a form that is immediately and directly related to the environment that the system or structure will be subjected to. Because of the extremely large number of materials, including variants subjected to different fabrication processes, and environmental conditions, it is too costly and nearly impossible to test all the combinations of

material and environment. The result is that it can be very difficult to find completely relevant data that substantiates a decision. Materials scientists over the years have devoted significant resources to corrosion testing and analysis.

Accelerated testing using salt spray or controlled humidity and temperature chambers are often used to investigate the potential for a material to corrode or a CP&C technology to function properly. Unfortunately, these tests don't replicate true operational conditions nor do they account for the synergistic affects of other contribution factors such as atmospheric pollutants or chemical exposure during service. This is what makes conducting a corrosion analysis such a challenge (Benjamin *et al.*, 1986).

Results of corrosion tests are usually reported as namely; loss in weight or reduction in thickness per unit of time; change in tensile strength; time-to-fracture (SCC); time-to-perforation, time-to-10%-increase-in-electrical-resistance, time-to-initial-rust, 10% rust, or complete rust. In some cases, changes in ductility, the reduction in thickness or penetration in microns per year **(µm/y)** or mils per year **(mpy)**is the most general and useful measurement of corrosion rate (Table 2.2).

2.6 Corrosion Protection and Control Methods

Even with the proper selection of base metals and well-designed systems or structures, there is no absolute way to eliminate all corrosion. Therefore, corrosion protection methods are used to additionally mitigate and control the effects of corrosion. Corrosion protection can be in a number of different forms/strategies with perhaps multiple methods applied in severe environments (Benjamin *et al.*, 1986). Forms of corrosion protection include the use of inhibitors surface treatments, coatings and sealants, cathodic protection, and anodic protection. This section discusses many of the various forms of corrosion protection methods.

2.6.1 Cathodic Protection

Cathodic protection (CP) is a widely used electrochemical method for protecting a structure or important components of a system from corrosion. A CP system is essentially an electrochemical cell and must have a cathode, an anode, an electrical connection between them and an electrolyte.

The principle behind CP is that dissolution of a metal (cathode) can be suppressed by supplying is with electrons, and in effect, controlling the corrosion. Corrosion is then targeted on the anode instead of the metal. Since an electrolyte is required for this method of protection, CP is not effective for systems in air or other environments that resist current flow between the anode and cathode.

There are two main classes of CP: active and passive. Active cathodic protection, also called impressed-current, requires the use of an external power supply. In this type of protection, the negative terminal of the power supply is connected to the metal to be protected, and the positive terminal is connected to an inert anode. The anode, however, is often not more anodic to the metal, and can be even more cathodic than the metal. The impressed-current ensures that current flows such that the metal acts as the cathode and is therefore protected from corrosion. Moreover, the anodes are not typically consumed by corrosion in impressed-current CP systems, since they do not undergo the typical corrosion reactions. It is possible to overprotect a system using impressed-current CP (Trethewey, and Chamberlain, 1995). If the voltage is too high, the metal can experience hydrogen embrittlement (e.g. steel) or possibly accelerated corrosion (e.g. aluminum). Therefore, proper conditions for the system should be determined in order to optimize the protection. Passive CP systems are simpler than impressed-current systems and

involve the galvanic coupling of the metal to be protected to a sacrificial anode, which corrodes preferentially. The anode in this type of system must be more anodic than the metal and must also readily corrode without passivation in order for the system to be successful. In some instances the sacrificial anode must be replaced after it has been consumed to ensure protection of the structure.

2.6.2 Anodic Protection

Anodic protection is a method of corrosion control that was developed more recently than cathodic protection, but it is used less frequently. As its name implies, anodic protection shields the anodic electrode in the system from corrosion rather than the cathodic electrode as in CP. The principle behind anodic protection, however, is not quite analogous to that of CP. Essentially, instead of shifting corrosion potential from the metal to be protected to an anodic material as in CP, anodic protection involves passivation of the metal to be protected. A passive film forms in the surface of the metal with the application of an electrical current. Once this film is formed, it acts to protect the metal from dissolution, and the film itself is nearly insoluble in the environment which it formed. Passivation causes metals to become very non-reactive and consequently very resistant to corrosion. The limitation of this type of corrosion control is that not every metal can be protected this way; only certain metals in specific environments can be anodically protected (Benjamin *et al.*, 1986).

2.6.3 Sacrificial Anodes

Sacrificial anode is also known as galvanic anode.They are easily corroded materials deliberately installed in systems to be sacrificed to corrosion, leaving the rest of the system relatively corrosion free. The mechanism of sacrificial anode protection system is very

similar to the reaction mechanism of electrochemical cells. In sacrificial anodes the protected metal is placed on the cathode side and the a more reactive metal or alloy (having a larger potential difference than the protected metal as an anode). The redox reaction will proceed spontaneously. An oxidation reaction occurs at the anode, which means that sacrificial metal will be consumed. At the same time, the reduction reaction occurs on the cathodic site, preventing the protected metal from erosion. Thus, corrosion on the protected metal is successfully shifted to the anode, protecting the metal.

The materials used for sacrificial anodes are either relatively pure active metals, such as zinc or magnesium or aluminum alloys that have been specially developed for use as sacrificial anodes. They are normally supplied with either lead wires or cast metal straps to facilitate their connection to the structure been protected either by welding or mechanical connections.

2.6.4 Surface Treatments

A surface treatment is the modification of a material's surface using various means to improve some characteristic of the material, in this case the corrosion resistance. Conversation coating and anodizing involves a chemical reaction to create an improved corrosion resistant oxide film layer on the metal's surface. Shot peening is a mechanical process to induce compressive residual stresses improving resistance to SCC and corrosion fatigue. Laser treatment uses heat to modify surface structure, aid a chemical reaction in modifying the surface, or to induce compressive residual stresses within a metal to increase it resistance to SCC and corrosion fatigue (Trethewey and Chamberlain, 1995).

2.6.4 Corrosion Inhibitors

Corrosion inhibitors are substance, which when added in small concentration to an environment, effectively reduces the corrosion rate of a metal exposed to that environment. The basic mechanisms by which inhibitors function include the followings;

(1) They absorb onto the surface of the corroding material as a thin film.
(2) They change the characteristics of the environment either by producing protective particulates or by removing or inactivating an aggressive constituent in the environments.
(3) They induce the formation of thick corrosion product, which forms a passive layer

Efficiency of inhibitor can be qualitatively related to the amount of absorbed inhibitor on the metal surface. The adsorption of inhibitor is governed by the residual charge on the surface of the metal surface physical or electrostatic and chemisorptions:

(a) **Physical or electrostatic adsorption**– is due the electrostatic attraction between the inhibiting ions or dipoles and the electrically charge surface of the metal. The forces in the electrostatic adsorption are generally weak. The inhibiting species adsorbed on the metal due to electrostatic forces can also be adsorbed easily. A layer of water molecule separates the metal from the ions. The physical adsorption process has low activation energy and is relatively independent of temperature.
(b) **Chemisorption –** is probably the most important type of interaction between the metal surface and an inhibitor molecule in corrosion inhibition system. The adsorbed species is in contact with the metal surface. The chemisorption process is slower than electrostatic sorption and has higher activation energy. The temperature dependency shows higher

inhibition efficiencies at higher temperature unlike electrostatic adsorption, it is specific for certain metals and is not completely reversible.

Corrosion inhibitors are substances which when added in small concentrations to corrosive environments decrease or prevent there action of the metal with the media. Inhibitors are added to many systems such as refinery units, cooling systems, pipelines, oil and gas production units. They are classified in various ways, although the widely known classifications are:

(1) **Cathodic Inhibitors**–Cathodic inhibitors reduce the rate of cathodic reaction namely oxygen reduction in near neutral environments and hydrogen evolution in acid solutions respectively. These form species that precipitate on cathodic sites and thus increase the surface impedance and lower the diffusion rate. The inhibiting action of cathodic inhibitors work by three mechanisms;

(a) Cathodic poisons: in this case, the cathodic reduction process is suppressed, for example by impeding the hydrogen recombination and discharge. But it, it may increase the tendency of the metal to be susceptible to hydrogen induced cracking. Hydrogen may absorb into the metal during this process. It is essential to keep hydrogen in atomic form. Typical types of cathodic poison are arsenic and antimony.

(b) Cathodic precipitates: compounds such as calcium, magnesium will precipitate as oxides to form a protective layer which acts a barrier on the metal surface.

(c) Oxygen scavenger: this mechanism functions by the removal of oxygen in the system to reduce corrosion. The compounds of oxygen scavenger react with oxygen presenting the system to form a product.

(2) **Inorganic inhibitors** –crystalline salt is the most and common extensive useof this group of inhibitors such as sodium chromate and molybdate. The only active groups of these compounds that functions to reduce corrosion are the negative anions they carry.

(3) Mixed Inhibitors–they are rarely used as a single compound only and its formulation can be composed of two or more inhibitors which all carry different characters. This is due to three factors:

(a) A single inhibitor can only inhibit a few numbers of metals. When the environment involve multi-metal system, the inhibitive action may sometimes cause jeopardizing effects to other metals

(b) Advantages from anodic and cathodic inhibitors can be combined and optimized for best performance

(c) Addition of halide ions improves the action of organic inhibitor in acid solution.

(4) Precipitation Inhibitors –These inhibitors are often film- forming in nature, precipitate on the metal surface, forming a protective barrier. Precipitation inhibitors such as silicates and phosphates are effective at blocking anodic and cathodic sites. Hard water is rich in magnesium and calcium. When these salt precipitate on the metal surface, for example at the cathode where the pH is higher, they establish a protection layer on the metal.

(5) Film- forming inhibitors–Its often distinguished by two classes. The first one works by slowing down the corrosion without stopping it completely. The second ceases the attack completely. However the efficiency of this inhibitor depends on the pH value and saturation index. The saturation index is then in turn determined by the water composition and temperature.

(6) **Volatile Inhibitors–**This type of inhibitors is also known as vapour phase inhibitors. As corrosion can also occur in vapour environment, it is useful to carry corrosion inhibitors into the system, which then need to be, themselves, volatile. When the inhibitor molecules in the vapour, comes into contact with the surface of a metal, the adsorption of the inhibitor will occur. The moisture then hydrolyses it, hence protective ions may be released. These include species like amines and nitrites for inhibition of ferrous metal.

(7) Passivating (Anodic) Inhibitors–Passivating inhibitors are anodic inhibitors. They cause the anodic curve of polarization to shift such that less current flows. They have the ability to passivate the metal surface. There are two categories of passivating inhibitors, namely oxidizing anions and non-oxidising anions.

Oxidizing anions such have the ability to passivate metal in the absence of oxygen. Typical oxidizing anions are chromate, nitrite and nitrate. Non-oxidizing ones such as phosphate, tungstate and molybdate require oxygen to perform passivation.This kind of inhibitor is by far the most widely used and possesses higher efficiency than others.

However, one major drawback of it is that in order to maintain sufficient passivation of the metal and thus providing sufficient inhibition, the concentration of the inhibitor must be kept well above a critical or minimum concentration. If the concentration is below the minimum value, it is likely that the metal, which is to be protected in to the first place, will suffer from localized corrosion such as pitting.

(8) **Organic Inhibitors**–Both anodic and cathodic effects are sometimes observed in the presence of organic inhibitors, but as a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Organic inhibitors,

usually designated as film-forming, protect the metal by forming a hydrophobic film on the metal surface. Their effectiveness depends on the chemical composition, their molecular structure, and their affinities for the metal surface. Because film formation is an adsorption process, the temperature and pressure in the system are important factors.

Organic inhibitors will be adsorbed according to the ionic charge of the inhibitor and the charge on the surface. Cationic inhibitors, such as amines, or anionic inhibitors, such as sulphonates, will be adsorbed preferentially depending on whether the metal is charged negatively or positively. The strength of the adsorption bond is the dominant factor for soluble organic inhibitors. These materials build up a protective film of adsorbed molecules on the metal surface, which provides a barrier to the dissolution of the metal in the electrolyte. Because the metal surface covered is proportional to the inhibitor concentrates, the concentration of the inhibitor in the medium is critical. For any specific inhibitor in any given medium there is an optimal concentration.

.2.7 Natural Products as Corrosion Inhibitor for Metals

Early success in the adoption of natural products as metallic corrosion inhibitors from the 5th century to the 15th century did not lead to its adoption by corrosion engineers and scientist, the use of natural products (flour, bran, yeast, a mixture of molasses and vegetable oil, and starch) for pickling of metal articles by master-armourers have been reported (Putilova*et al.,* 1960; Sanyal, 1981). During, the 1970s and 80s, there was an increase needs of natural products as corrosion inhibitors due to mild enforcement of the laws, which harness the use of eco-friendly inhibitors owing to toxicity and the environmental hazards with the use of chromates inhibitor (Ebenso, 2011).

At the inception of the new millennium, sustainability research has been increasingly accepted and plays a pivotal role to conservation of the environment by the development of more efficient and environmentally friendly corrosion inhibitors. Sustainable development is thus the natural trend of green inhibitors, but not an independent factor from economic growth, quality of human life and health care (Ebenso, 2011). A number of natural products have been reported as corrosion inhibitors, an increased interest is still being continued, resulting in enormous data on plant extract as corrosion inhibitors (Ebenso, 2011). The reason for this uninterrupted interest can undoubtedly be ascribed to an increased awareness on the safety and environmental issues of corrosion inhibitors arisen in the industries been of global concern.

Recently, many alternative eco-friendly corrosion inhibitors have been developed through green approaches. This clearly shows that the era of development of "green" alternatives to combating corrosion is here, green approaches to corrosion mitigation entail the use of substances, techniques, and methodologies that reduce or eliminate the use of/generation of products, by-products, solvents, reagents, and so forth that are hazardous to human health or the environment in combating corrosion.

Sabgeetha*et al.* (2011) noted that while new and sustainable materials are continuously being developed and research. plant scientists look for renewable and suitable possible ways that if plant materials are used as alternate corrosion inhibitors, to prevent the corrosion of metals, the plant Kingdom will slowly diminish; Metals will be protected at the cost of destruction of plant Kingdom, which call for greater concerns among scientists despite the several factors including cost and amount, easy availability and most important safety to environment and its species due to the ecological awareness and environmental strict regulations, consequently the need to

develop environmentally friendly processes need to be considered when choosing an inhibitor (Amitha*et. al.,* 2012).

2.8 Recent Advances on Natural Products as Corrosion Inhibitor for Metals

Several research efforts on sustainability of plant extract as efficient and effective corrosion inhibitors has been widely reported in the literature, irrespective of the type and part of plant, with the exact mechanisms involved in inhibition process, the formation of corrosion scales is a major controlling factor in corrosive medium and various plant extracts have individual corrosion mechanisms in different medium (Aku *et al.,* 2006; Ebenso *et al.,* 2011; Alaneme and Olusegun 2012; Ayeni*et al.,* 2012; Abdulwahad*et al.,* 2013; Omotoyinbo*et al.,* 2013).

Sharma and Kirti (2014) studied the inhibitive properties of *Heliotropium indicum* leaveextracts on the corrosion inhibition of aluminum in 1.0M H_2SO_4 solution using weight loss data and thermodynamic techniques. The studies proposed the absorption mechanism to be physisorption and obeyed Langmuir isotherms. The chemical, kinetic and thermodynamic studies of the reactions showed *Heliotropium indicum* leaf extracts exhibit good corrosion inhibitor properties and contained oxygen, nitrogen, and sulphur atoms in their structure.

Madufor*et al.*(2013) extends the growing interest on environmentally friendly corrosion inhibitors in studying corrosion inhibition of aluminium in 1.5M H_2SO_4 solutions by 95% fruit ethanol extract from *Chrysophyllum albidum* using weight loss and thermometric techniques at temperature range of 30 – 60^oC after 168 h of immersion period. The concentrations of inhibitor (fruit extract from *Chrysophyllum albidum*) prepared and used in the study were in the range 0.1 – 0.5 g/l. as reported, the weight loss experiments show a reduction in weight loss of the metal coupons in the presence of the inhibitor (*Chrysophyllum albidum* fruit extract)

compared to the free acid solution (blank) and loss in weight of the coupons decreased with increase in the concentration of the inhibitor was observed. Similar trend was reported for other temperatures but with greater values of weight loss in thermometric techniques.

However, it was reported that the inhibition efficiency increased with increasing concentration of the *Chrysophyllum albidum* fruit extract. The maximum inhibition efficiency was observed to be 40.52% at 0.5g/l and fits into Temkin adsorption isotherm on the aluminium surface. The inhibiting effect of the *Chrysophyllum albidum* fruit extract was adsorbed on the surface of the aluminiumand reported to be attributed to the presence of the phytochemical constituents (Edem et *al*., 1987).

Yaro *et al.* (2010) through experimental studies determined the efficient of synthetic magnetite and ferrous gluconate as inhibitors for oil-well steel rig-site in 50 mg/l sulphide concentration in varying parameters such as pH ranging from 5.5 to 11.5, and High Temperature High Pressure (HTHP) conditions by the weight loss method. The ferrous gluconate was found to give a higher corrosion inhibition compared to the synthetic magnetite form up to 99.2% efficiency. Although, synthetic magnetite gives an optimum inhibition efficiency (IE) up to 75.1% at the ratio of the sulphide to scavenger form 1:4 at the lowest pH of the experiment (pH 5.5), the ratio was concluded not desirable for a drilling mud, so ferrous gluconate found to be a better corrosion inhibitor in 50mg/l concentration sulphide solution. As the pH increases, the inhibition efficiency of the magnetite decreases and found to be lowest at the alkaline pH of 11.5.

Anafi and Obi (2004) investigated the corrosion inhibition of low carbon steel in simulated media using plant leaf extracts. The solvent (methanol) extract of bitter leaf was compared with sodium benzoate on low carbon steel in stimulated media such as sea water, 0.3 M H_2SO_4 and

0.3M HCl media using weight loss method techniques. The maximum bitter leaf inhibition efficiency reported in sea water was at 61.19%, however Sodium benzoate surpassed bitter leaf in its corrosion inhibition ability in all test media used in the investigation

Yawas (2005) assess the suitability of natural products such as neem, mahagony, cashew, locust bean husk, and acacia nilotica pod extracts as corrosion inhibitors. The Inhibition efficiencies increased with increase in inhibitor concentrations and temperature but decreased in the case of cotton seed and sesame oil which showed the ability of the inhibitors to reduce stress corrosion of carbon steel in acidic media.

Suleiman*et al.* (2012) predicted the suitability of biodegradable organic materials as corrosion inhibitors on mild steel in 0.5m sulphuric acid using surface morphology analysis and characterization on exposed samples by scanning electron microscope (SEM). The active films formed on the surface of the mild steel by optimum organic extract in acidic medium plant extract exhibits smooth surfaces in the presence of the inhibitor, while in the absence of inhibitor becomes more susceptible to attack in the corrosive medium, in comparisons to previous research by Ostovari*et al*. (2009) and Lebrini*et al.* (2011) similar results was observed.

Nnabuk*et al.* (2014), studied inhibition and adsorption properties of *Commiphoraafricana*gum on aluminum using quantum chemical study and FTIR corrosion products analysis. The chemistry energy study reveals that the inhibitors adsorption on metal surface is spontaneous, exothermic and best fitted the Langmuir adsorption model, while 3-diol gave the highest inhibition efficiency and potentials. Also, from the qualitative studies, it was observed that functional groups such as dihex-5-en-2-yl phthalate and 2-(hydroxymethyl)-2-nitropropane-1,3-

diol and dihex-5-en-2-yl phthalate and 2-(hydroxymethyl)-2-nitropropane-1 are present as active constituents in the gum,

Arthur*et al.* (2014) studied the inhibitive properties of *Anarcadiumoccidentale*gum on mild steel in 0.1 M H2SO4 using gravimetric technique, it was reported that cashew gum adsorption mechanism is physisorption and serves as good corrosion inhibitor. Also the experimental data complied with the Langmuir adsorption isotherm, thus its inhibition efficiency potential increases with increase of concentration of the gum, while its corrosion rate decreases with increase addition of the gum was 88% obtained at 1.0g/250cm3 volume of Cashew gum. Also, the adsorption of gum on mild steel surface is spontaneous attributing that fact to its low value of energy of adsorption and supports the mechanism of physical adsorption.

Although, many researchers had worked on plant extracts using different metals, to mention a few such as steel and its alloys (Yaro *et. al*., 2010 ; mild steel and N80-steel, Loto*et al.,* 2011; austenitic stainless steel;), aluminium and its alloys (Nnabuk,*et al.,* 2014; aluminium, Ebenso, *et al.,* 2011 (AA 1060-aluminium alloy), brass (Loto*et al.,* 2011; duplex brass) nickel, zinc (Olorutoba, *et al.,* 2014; zinc plated) and composite (Yaro *et al.,* 2010; Al-5%Si/15%Sic metal based composite), the inhibitive properties of *Chrysophyllum albidium*and*Heliotropium indicum leave extracts as inhibitors on*medium carbon low alloy steelin 1M HCl and 1M H_2SO_4 solution respectively using electrochemical technique has not been reported in literature. This is the thrust of this work and focused on *Heliotropium indicum* and *Chrysophyllum albidium* plants, with a view to studying its inhibition efficiencies and mechanism on corrosion of medium carbon low alloy steel in 1M HCl and 1M H_2SO_4 acidic media.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1.1 Materials: The materials used for this research work are listed below:

(1) 19mm medium carbon low alloy steel rod
(2) Aerial parts of *Chrysophyllum albidium*and*Heliotropium indicum* plants
(3) 2.5 litreseach of Fishers certified (UK) Hydrochloric and sulphuric acids
(4) 60cl Shell Ensis Fluid SX *and* 85 litres Distilled water
(5) 2.5 litres of Acetone and 7.5 litres of Ethanol (BDH grade)

3.1.2 Equipment: The equipment used for this research work includes:

(1) Emission Optical Spectrometer
(2) Nikkon Metallurgical Microscope (Model: NJF-20A)
(3) Soxhlet Apparatus
(4) Scanning Electron Microscope
(5) Ultraviolent-visible Spectrometer (Model: Hitachi F-4500)
(6) ShimaduFourier Transform Infrared Spectrophotometer (Model: 8400S)
(7) Digital pH meter (Model: pHS-25)
(8) Brooks Universal Hardness Tester (Model: CRBD)
(9) Izod Impact tester (120 Foot pound)
(10) Hounsfield Tensometer (20KN)
(11) Automated Digital Viscometer (Model: KV DV-1)
(12) Potentiostat equipped with platinum electrode (Model: P-50)
(13) Polishing Machine
(14) Incubator and Muffle Furnace
(15) Digital top loading Balance (Mettler P-160N)
(16) Vacuum Rotary Evaporator

3.2 METHODS

3.2.1 Design of Experiment

Experimental design for plants and number of specimen used in the research work is as follows:

Table 3.1: Summary of the notations adopted for experimental design

Notation	Meaning
A	Crude extract of African Star Apple (*Chrysophyllum albidium*) Leaves
A1	Protective film of African Star Apple (*Chrysophyllum albidium*) Leaves
B	Crude extract of Cock's Comb (*Heliotropium indicum*) Leaves
B1	Protective film of Cock's Comb (*Heliotropium indicum*) Leaves
C	Shell Ensis SX (SE) used as Standard Inhibitor

Table 3.2: Summary of number of specimens adopted forexperimental procedures

Activity	Study	Before Corrosion Test	After Corrosion Test	Total
Chemical Composition and Microstructural Examination	Chemical Analysis	1	-	1
	SEM Analysis	1	4	5
	Microstructural Examination	1	-	1
Mechanical Test	Hardness Value	1	8	9
	Impact Strength	1	8	9
	Tensile Strength	1	8	9
Corrosion Test	LPR Method	-	32	32
	Weight Loss	-	356	356

3.2.2 Chemical Analysis of As-received Low Alloy steel

The as-received medium carbon low alloy steel rod of 19mm (diameter) procured from the metal market at Owode-Onirin Lagos, was subjected to spectrochemical analysis adopting Fe-10-ASML methods in accordance with ASTM E415 standard using Emission Optical Spectroscopy (Model No: LMM05).

3.2.3 Microstructural Examination of As-received Low Alloy Steel

The microstructure examination of the as-received medium carbon lowalloy steel was carried outaccording to ASTME340 using the Metallurgical Microscope. The steel sample of 19mm (diameter) were sectionedand polished with abrasive papers of successive finer grade (240, 320, 400, 600, and 800),and further swabbed in Nital etchant solution. The microstructure obtained was recorded using a high resolution Metallurgical Microscope at (x200) magnification.

3.2.4 Plant collection and Identification

Aerial parts of the plants (Plate 3.1a) comprising of the leaves, stem and flowers were collected and identified as *Chrysophyllum albidium (*Family: Sapotaceae) and *Heliotropium indicum* (Family: Boraginaceae) with Voucher number2680 and 1007 respectively at the herbarium unit, Department of Biological Sciences, Ahmadu Bello University, Zaria, Nigeria.

The leaves (Plate 3.1b) were carefully removed from their plant; washed, air-dried under shade for 7 days, ground into fine powdered and stored at room temperature in a closed container for further use.



Plate 3.1: Photograph of (a) Aerial parts(b) leaves plants(Source: Botanical garden ABU, 2015)

3.2.5 Biochemical Extraction

Extracts of*Chrysophyllum albidium*and *Heliotropium indicum*plant leaves were extractedin accordance with standard method ofextraction adopted from Yawas (2005) using the Soxhlet apparatus (Figure 3.1), which consisted of round bottom flask, thimble, extraction chamber, condenser and siphon arm.

290g dry fine powder of the *Chrysophyllum albidium*and *Heliotropium indicum*plant samples were placed inside a thimble made from filter paper and loaded into the extraction chamber of Soxhlet apparatus, attached to a round bottom flask containing a solvent (ethanol) and a condenser. The solvent was heated to evaporation. The hot solvent vapour travelled up to the condenser, where it cools and drizzled on the dry powder inside the thimble. The chamber containing the powder slowly fills with warm solvent and then emptied by siphon action, back down to the flask.

This cycle is allowed to repeat untilall the ground leaves were completely extracted in the lower flask. During each cycle, a portion of the material dissolves in the solvent until the entire

leaching was completed. The extracted compounds was concentrate and excess solvent were removed using a vacuum rotary evaporator, leaving behind only the crude extracts (bioactive extracted compounds) and scrap with the use of metal scraper into a beaker, covered with aluminium foil and stored in desiccators for further use. The percentage yield was determined with reference to the weight of the ground leaves (equation3.1).

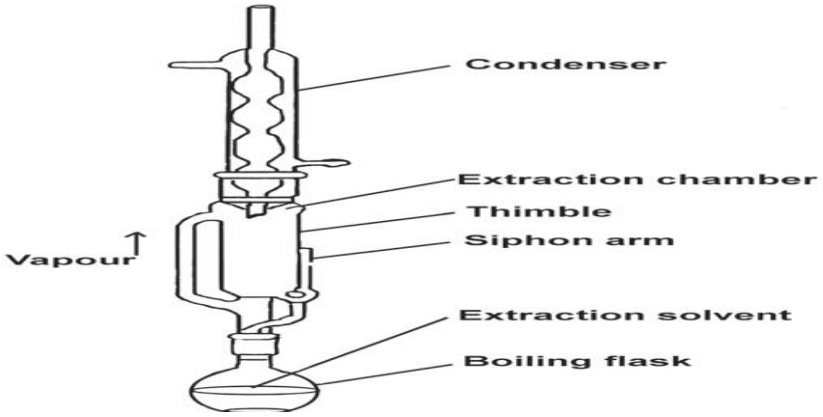


Fig. 3.1: Schematic Diagram of the Soxhlet Apparatus (Source:Vattuone, 2009)

$$\%(w/w)Yield\ of\ extract = \frac{Weight\ of\ Total\ extract}{Weight\ of\ powdered\ Material} * 100 \quad \ldots\ldots\ (3.1)$$

3.2.6 Phytochemical Screening

Phytochemical screening was carried out in accordance with standard laboratory procedure of the plant sampling preparation techniques (2009) and AOAC (1990) method for the determination of bio-active and chemical constituents such as tannins, flavonoids, glyseroids, steroid, tripenenes, alkaloids and saponinspresent in plant extracts; tests solution was prepared by dissolving one (1) grams of bio-extracts using distilled wateras reported byEvans (1996).

(1) Test for Alkaloids

Qualitative phytochemical screening for alkaloids was carried out using Dragendoff's test; three (3) drops of drangendoff reagents added to 40ml of dissolved bio-extracts solution in a test tube. A reddish brown precipitate indicates presence of alkaloids (Evans, 1996) while quantitative phytochemical determination of alkaloids was carried out using Harborne (1998) gravimetric method; 5g of ground powdered sample was dispersed in 50 mL of 10% acetic acid in ethanol, filtered and the filtrate was evaporated to 15 mL of its original volume in a water bath. Further, precipitated with a drop of ammonium hydroxide and the precipitates were recovered by centrifugation at 1000rpm for 10 minutes, dried at 700^{o}C for 30 minutes in a vacuum oven. The Percentage alkaloids were calculated using the following relationship:

$$\%\ Alkaloids = \frac{Weight\ of\ dried\ precipitate}{Weight\ of\ original\ ground\ sample} * 100 \ldots\ldots (3.2)$$

(2) Test for Tannins

Qualitative phytochemical screenings for tannins was carried out using ferric chloride test; 3 drops of ferric chloride solution were added to 40ml of dissolved bio-extracts solution in a test tube. A greenish black indicates presence of condensed tannins while hydrolysable tannins give a brownish-blue precipitate (Evans, 1996) while quantitative phytochemical determination of tannins were determined using Harborne (1980) method; 2g of ground powdered sample was poured into a beaker containing 50 mL distilled water and heated to 60^{o}C, thereafter filtered and residue discarded. 10 mL of 4.0% copper acetate solution was added to the hot filtrate and boiled for 10 minutes. Further, precipitated with filter paper and the residue was driedand weighed into a crucible incinerated in a muffle furnace at 600^{o}C. The Percentage total soluble tannins were calculated using the following relationship:

$$\%\ Total\ soluble\ tannin\ = \frac{Weight\ loss\ after\ ashing}{Weight\ of\ sample\ before\ ashing} * 100 \ldots\ldots\ldots\ldots\ldots (3.3)$$

(3) Test for Flavonoids

Qualitative phytochemicalscreening for flavonoids was carried out using sodium hydroxide test; three (3) drops of 10% sodium hydroxide added to 40ml of dissolved bio-extracts solution in a test tube. A yellow colouration was noticed which indicates presence of flavonoids (Evans, 1996) while quantitative phytochemical determination of flavonoids was conducted using Allen *et al.* (1973) gravimetric method in which 10g of ground powdered sample was digested with 100ml of 80% aqueous methanol at room temperature, thereafter filtered and the residue was weighed into a crucible and dried to a constant weight in the oven. The Percentage flavonoids was calculated using the following relationship:

$$\%\ Flavonoids\ = \frac{Weight\ of\ dried\ residue}{Weight\ of\ initial\ sample} * 100 \ldots\ldots\ldots\ldots\ldots (3.4)$$

(4) Test for Saponins

Qualitative phytochemical screening for saponins was carried out using frothing test in which 10ml of distilled water wasadded to 0.5mg of bio-extracts and shaken vigorously.After, the test tube was allowed to stand in a vertical position and observed for up to 30 minutes.Honeycomb froth was noticed and persists for upto 12 minuteswhich indicates presence of saponins (Evans, 1996).

Quantitative phytochemical determination of saponins was carried out using Association Official Analytical Chemists (1990) method in which2g of ground powdered sample in triplicate werefolded in a filter paper and put in a soxhlet apparatus thimble for 3hrs refluxing with 100

cm^3 acetone and methanol in a $250cm^3$ and $150cm^3$ capacity flask respectively. Weight of before and after the second extraction was noted and taken as the change in weight, methanol was recovered by distillation and the flasks oven dried, allowed to cool at room temperature and weighed. The Percentage saponins contents were calculated using the following relationship:

$$\%\ Saponin\ \left(\frac{mg}{100g}\right) = \frac{A-B}{Weight\ of\ initial\ sample} * 100 \ldots\ldots\ldots\ldots\ldots (3.5)$$

Where A= mass of flask and extract (g) and B= mass of empty flask (g)

(5) Test for Steroids and Triterpenes

Qualitative phytochemical screening for Steroids and Triterpenes was carried out using Lieberman-Bucchard test;in which equal volume of acetic acid anhydride was added to 20ml of dissolved bio-extracts solution in a test tube and mixed gently. 1ml of concentrated acid was added to the side of the test tube to form a lower layer and colour changes were observed immediately. A strong interface of blueish (upper) and reddish (down) ring was seen and formed layer which indicates presence of steroids and triterpenes.

3.2.7 Physico-chemical Analysis

(1) **Determination of Physico-chemical Properties**

The physicochemical parameters such as colour, pH, appearance and solubility were determined in accordance with the standard procedure ofAssociation Official Analytical Chemists(1990) while density and viscosityin accordance to the ATM D1298 and Newtonian fluid methods respectively. The results of the tests are presented in Table 4.5 and Figure 4.2.

The colour determination of the plant extracts was determined using the visual comparison method at the earliest extraction time because physical changes occurring in the storage may affect the colour. 1.0 g of the extracts was added to 50 mL of deionized water at ambient temperature and viewed under transmitted specular light reflection at an angle opposite to the incident light through a depth of several diffuse light-reflections. The apparent colour of the sample was observed moving eyes focused away from the glare (specular) and concentrate on examining the diffuse (scattered) reflectance from the sample (ASTM D 1729). The Odour of the extracts was determined using sight and smelling techniques as reported by Amira *et al.* (2014).

The solubility of the plant extracts was determined in cold water, hot water, acetone, and ethanol. 1.0 g of the extracts was added to 50 mL of the respective solvents and left overnight. 25 mL of the clear supernatants were taken in small pre-weighed evaporating dishes and heated to dryness over a digital thermostatic water bath. The weight of the residue with reference to the volume of the solutions were determined using a digital top loading balance (Mettler P-160N) and expressed as the percentage solubility of the extracts in the solvents as reported by Eddy *et al.* (2014) and Anema *et al*. (2006).

While the pH of the extracts was determined by shaking 1% w/v (0.5g in 50mLof distilled water) dispersion of each of the sample in water for 5 min and the pH was measured using a pre-calibrated digital pH meter (Model pHS-25). The electrode of the pH meter was immersed into the dissolved solution at ambient temperature and the pH value was read directly through the digital meter's read out system.

The kinematic viscosity of the plant extracts was determined by dissolving the extracts in distilled water, the dissolved samples was filled up to the marked level of 10ml on the cylinder

with 20ml capacity, covered with a T-shaped spindle metal ensured to touch the sample at the marked level and the narrow part of the spindle was fixed to the viscometer system while the bottle end of the cylinder was screw covered with another metal disc to another container in the viscometer to hold the metal cylinder containing the test samples. The dissolved plant extracts was treated as a Newtonian fluid using the automated digital viscometer (Model: KV DV-1) at a same speed and spindle number for 5 minutes, readings were obtained directly from the automated viscometer scale in centipoise (1cP = 1 mPa·s) with aid of a liquid in glass thermometer placed inside a regulated control water bath (Adindu*et al.*, 2003; Nwosu*et al.*, 2014). The dynamic viscosity (μ) can be obtained by multiplying the kinematic viscosity (v) by the density ρ of the liquid (ASTM D445).

(2) Biodegradable tests

The biodegradation tests was carried out using closed bottle (oxygen demand) testsin accordance with OECD 306 Marine BOD (2005) model adopting the Azide modification of the Winkler method.Standard test solutions of each inhibitor were prepared by dissolving 0.5g formulations in 1000ml of distilled water, after a dilution factor of 1:10 was made and used for BOD test. The Biochemical Oxygen Demand (BOD) of each inhibitor was calculated using the relationship:

$$\text{BOD (ppm)} = \frac{(DO_1 - DO_2)}{P} \quad \text{……..} \quad (3.6)$$

Where: DO_1 = Dissolved Oxygen of diluted sample immediately after preparation, mg/L,
DO_2 = Dissolved Oxygen of diluted sample after incubation period at 20°C, mg/L,
P = dilution factor (1:10)

3.2.8 Proximate Analysis

The proximate analysis was carried out out using the methods described by Ureigho and Ekek (2010)performed at the Institute for Agricultural Research, Samaruin order to estimate the various food parameters such as moisture content, ash content, crude fibre, crude lipid, crude protein, and carbohydrate presence in the plants leaves.

(i) Determination of Moisture contents

5.0g of each ground sample was dried in a weighing bottle to constant weight at 100^{o}C in an electrical oven for 12 hours, then reweighed several times until a constant weight was obtained. The Percentage moisture content was calculated using the following relationship:

$$\%\ Moisture\ Content = \frac{Weight\ of\ original\ sample - weight\ after\ drying}{Weight\ of\ original\ sample} * 100 \ldots\ldots (3.7)$$

(ii) Determination of Ash contents

This was determined by the dry-ashing method. Crucibles used for ash content determination were weighed and dried in an oven at 110 ^{o}Cto a constant weight. 5.0g of each ground sample was weighed and placed in the crucible, then the weight of the crucible and samples were taken. The crucible was placed in a muffle furnace and heated to 550^{o}C and kept for 3 hours to obtain a cotton wool like texture residue. The residue remaining after heating was weighed and taken as the ash content.

(iii)Determination of Fibre Contents

5.0 grams of the sample was placed in a beaker containing 1.2ml of H_2SO_4 in 100ml of solution and boiled for 30minutes, the residue was filtered and washed with hot water, the residue was transferred to a beaker containing 1.2gram of NaOH in 100ml of solution and boiled for 30minutes, the residue was washed with hot water and dried in an oven and weighed (C2), the

weighed sample was incinerated in a Furnace at 55O^{O}C, removed and allowed to cool, and weighed (C3). The % of Fibre was calculated using the following relationship:

$$\%\ Fiber\ = \frac{Weight\ of\ original\ sample\ (C2) - weight\ after\ incinerated\ (C3)}{Weight\ of\ original\ sample} * 100 \qquad \ldots\ldots (3.8)$$

(iv) Determination of Protein Contents

1.0g of the samples was weighed into the Kjeldahl flask while 0.1g of Ca2SO4 and 1.0g K2SO4 were added into the flask with 20ml of concentrated H2SO4. The flask was then placed in a slanting position on the Kjeldahl digestion heating mantle in the fume cupboard. Digestion continued until solution assumed color changefrom black to bluish-green. It was set up against blank, the digest were removed and allowed to cool and was then diluted with water and made up to 200ml on ice. 50ml of aliquot of each digest were poured into a distillation flask. 50ml of NaOH were carefully layered into the solution in order to make it a strong alkaline, and 50ml of 0.1N H2SO4 measured and kept in a beaker with two drops of methyl red as an indicator. The H2SO4 acted as a receiving flask. 150ml was distilled over then distillation was stopped by removing the solution in the receiving flask before the heat was put off to avoid drop in pressure. The distillate (excess acid) was titrated with 0.1M NaOH in the burette. This was done for all samples and blank and percentage protein was calculated.

(v) **Determination of Carbohydrate Contents**

5.0g of ground sample was digested with perchloric acid. Hydrolyzed starches together with soluble sugars were determined colourimetrically by the Anthrone method and expressed as Carbohydrate.

3.2.9 UV and FTIR Analysis of Plant Extracts

UV-Visible adsorption spectrum of the crude extracts was recorded with a Hitachi F-4500fluorescence spectroscopy. The results for the UV-Visible absorption studies of the extracts are presented in Appendix IV.

Identification of the active compounds present in the extracts and nature of the films formed on the surface of the metal specimens was conducted in accordance with the standard laboratory procedure 183W324 using Fourier Transform Infrared red spectroscopy. The sample was mixed withKBrsalt, using a mortar and pestle, and compressed into a thin pellet. Infrared spectra were recorded on*FT-IR*Spectrophotometerequipped with ZnSe optics and aDirect Trunk Group Selection(DTGS) detector and compared with those corresponding to pure compounds obtained in the same conditions (between a frequency range of 4000cm-1 to 400cm-1 resolution and 200 scans) as available for mass spectra data base at the department of Chemistry, Ahmadu Bello University, Zaria.

3.2.10 Preparation of Low Alloy steel for Corrosion Coupon

Coupons were prepared as recommended by NACE standard RP0775 (2005) for corrosion testing. The steel rods were machined to required dimension with diameter of 19mm and thickness of 15mm. the machined samples were polished using abrasive paper of 60; 120; 220; 320; 400; 600 and 800 grades. The polished coupons were washed with ethanol, conditioned with distilled water and allowed to dry in the air and then preserved in a desiccator charged with silica gel.

3.2.11 Preparation of Test Solution

(a) Preparation of HCl and H_2SO_4 Concentration

1M HCl and H_2SO_4 were prepared from Fishers certified analytical grade solutions with appropriate distilled water according to Yawas (2005) as shown in Appendix I.

(b) Preparation of various inhibitor concentrations from the plant extracts by successive dilution

Inhibitors of concentration of 100ppm; 200ppm; 300ppm; 400ppm; and 500ppm solutions were prepared from plant extracts and standard inhibitor (Appendix II).

3.2.12 Corrosion Tests

Traditional weight loss method andlinear polarization resistance methods of corrosion test were employed.

(1) Gravimetric Based Mass Loss Method

Coupons were suspended in the corrosion solutions with the aid of a thread in each beaker. The coupons were exposed for a period of 504 hours with 7 measurements taken at an interval of 72 hours. The weight loss were measured and then converted to corrosion rate (CR)using the relationship:

$$Corrosion\ Rate\ (CR) = \frac{87.6 * W}{\rho * A * t}(mmpy) \quad \text{.....} \quad (3.9)$$

Where W = *weight* loss of test coupon(mg),

ρ =density of the metal (g/cm^3),

A =exposed area of the test coupon (cm^2),

t =time for which the coupon is exposed (hrs.).

Inhibition efficiency was calculated using equation 3.10a and degree of surface coverage using equation 3.10b:

$$IE\ (\%) = \frac{CR_o - CR}{CR_o} * 100 \quad \text{.....} \quad (3.10a)$$

Degree of $Surface\ (\varnothing) = \frac{CR_o - CR}{CR_o}$ ……. (3.10b)

Where: $CR_o\ and\ CR$ are the corrosion rates without and with inhibitor

I.E and $(\varnothing)$ are Inhibition efficiency and degree of surface covered

The results of weight loss experiment are presented inFigures 4.8 - 4.25. Thermodynamic parameters as heat of adsorption of the inhibitor on the metal surface (Q), change in free energy of the reaction (ΔG), corrosion rate (CR) and energy of activation for corrosion reaction (E_a) were calculated using the Arrhenius equation (equation 3.11) and results are presented in Figures 4.26 – 4.37 and Table 4.8:

$$Log\ \frac{\mathrm{R1}}{\mathrm{R2}} = \frac{E_a}{2.303\ R} \quad \text{……. (3.11a)}$$

$$\nabla G\ (ads) = -RT \ln 55.5K \quad \text{……. (3.11b)}$$

$$K\ = \frac{\emptyset}{C\ (1-\emptyset)} \quad \text{……. (3.11c)}$$

Where: R_1 and R_2 are the corrosion rates at any given two different temperatures,

K refer as Equilibrium constant,

θ as the degree of surface coverage,

C as the concentration of inhibitor

The absorption mechanism and behaviour of active functional groups present in the bio-extracts were investigated at four different temperatures viz 303K, 313K, 323K and 333K. They were tested on commonly used absorption isotherm such as Langmuir, Temkin and Freundish isotherms and described with the best absorption isotherm (Figures 4.38 – 4.43).

(2) Linear PolarizationResistance Studies

Linear polarization test was carried out according to the standard of ASTM G59-97 using AC Potentiostat device. The electrochemical cell consisted of three electrodes: a saturated calomel reference electrode, a platinum auxiliary electrode (model: PP-50), and the prepared coupon as working electrode.

Samplesembedded in epoxy resins with an exposed area of 0.87 cm^2, served as working electrode and wasplaced in electrolyte cell fills with 200 ml of 1M HCl and H_2SO_4 acid solutions, equilibrate to generate electrochemical measurements at constant time of 15minutes including, long-term linear polarization resistance (LPR) and 1mV/s^{-1}scanning rate during polarization.

The first sets of electrochemical investigation were carried out without inhibitor to serve as control, subsequently in test solutions of prepared inhibitors of 100ppm; 200ppm; 300ppm; 400ppm; and 500ppmconcentrations.

The polarization resistance (Rp) values were determined using Tafel extrapolation method according to Stern Geary equation (equation 3.12):

$$I_{corr} = \frac{\beta_a \beta_c}{2.303\,(\beta_a + \beta_c)} {}^{1}\!/_{R_p} \quad \text{..... (3.12)}$$

Since LPR measurements to be carried out by polarizing the specimen from +25 to_25 mV with respect to Ecorr, at a determined scanning rate of 1mV/s_1.

Inhibition efficiency (IE%) were calculated using corrosion density (Icorr) measurements according to relationship (equation 3.13):

$$IE\ (\%) = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} * 100 \quad \text{..... (3.13)}$$

Where: $I_{corr}$is the corrosion current density and measured in solutions without inhibitor

$I_{corr\ (inh)}$) determined in solutions containing inhibitor

3.2.13 SEM Analysis

Scanning Electron Microscope (SEM) images at magnification of 4000 was used to observe thesurface morphology of the couponsbefore and after corrosion test. The images for SEM analysisof the coupons before and after corrosion test are presented in Plates 4.2 – 4.5 and Appendix V.

3.2.14 Determination of Mechanical Properties

Mechanical properties (hardness, impact and tensile strength) of the steelsamples before and after corrosion tests werealso determined using Rockwell Hardness Testing Machine, Izod Impact testing machine, Automatic Universal Testing Machineand Hounsfield Tensometer. The results are presented in Figure 4.7, Plate 4.1 and Tables 4.13 – 4.15.

(1) Hardness ValuesDetermination

The hardness values were determined in accordance with the ASTM E140 standard using the Brooks universal hardness tester (model: CRBD).Specimens were cut to required dimensionsof 19mm (diameter) and 15mm (thickness) wereplaced on the anvils of the machine with a diamond ball indenter of 2.5mm diameter,under minor and major loadsof 10kg and 187.5kg respectively. The minor load was applied to establish a zero datum position and then subjected to the major load. This loading process was repeated on three different positions on the specimen and the average values reading from the digital display of the hardness machine (HB Scale) were computed as the hardness value.

(2) Impact Testing

The impact tests were conducted according to ASTM A370 standard using the Izod impact machine of capacity 120 Foot pound.Prepared specimens of 12mm (diameter) and 60mm (thickness) given a notched of 1mm depth at the center were first positioned in the vice of the impact testing machine such that impact is transverse to the (anatomic) longitudinal direction and strikes by two released pendulums in opposite direction from their calibrated standard height to fracture of the specimen. The energy resistance of the specimen fixed in a cantilever position by means of a vice during this Izod pendulum impact was registered on a dial scale and generated for the impact values.

(3) Determination of Tensile Properties

The tensile tests were conducted in accordance with the ASTM E8-04 standardusing the Hounsfield tensometer of capacity 20kN. Specimens were cut to required dimensionsas follows 7.5mm of outside diameter with 5mm of inside diameter by 37mm of outside height with 31mm inside height (Appendix VI). Further, specimens were mounted and gripped in between the chucks of hydraulic controlled load system of the extensometer. The initial gauge length and diameter were recorded andsuccessive loadwere applied to tension. The load against extension graph was plotted andtraced out by thetensile machine thereby computing values for the yield and ultimate stress; yield and ultimate load; % reduction area and % elongation area.

CHAPTHER FOUR

4.0 RESULTS AND DISSCUSION

4.1 Chemical analysis of As-received Low Alloy Steel

Table 4.1: Chemical analysis of the as-received low alloy steel

Chemical Composition (%W)	
Iron (Fe)	97.860
Carbon (C)	0.5000
Manganese (Mn)	0.7760
Copper (Cu)	0.2010
Chromium (Cr)	0.1700
Nickel (Ni)	0.0848
Silicon (Si)	0.0214
Molybdenum (Mo)	0.0165
Cobalt (Co)	0.0131
Phosphorous (P)	0.0120
Arsenic (As)	0.0120
Aluminium (Al)	0.0025
Zinc (Zn)	0.0014
Tin (Ti)	0.0014
Tellurium (Te)	0.0110
Others	> 0.015

The results of the chemical analysis of the as-received steel sample shown in Table 4.1 revealed that Iron constitutes the highest amount of concentration up to 97.86%, while Manganese and Carbon exists as the major alloying element, present up to 0.776 and 0.5 percent. Also, the as-received steel sample had Silicon (0.241), Copper (0.2010) , Nickel (0.0848) and Chromium (0.170) combined as inter-metallic compounds with Iron and conform to specification of medium carbon low alloy previous identified by Alaneme and Olusegun (2012). Elements as defined

(Table 1) such as Si,Mo,Co, P, As,Al, Zn, Ti, and Te were insignificantly present in the low alloy steel. Other include elements such as Niobium (0.0015), Antimony (0.0095), Boron (0.00054) and Lanthanum (0.0014) were found to be present.

4.2 Mechanical Properties and Microstructural Examination of the As-received Sample

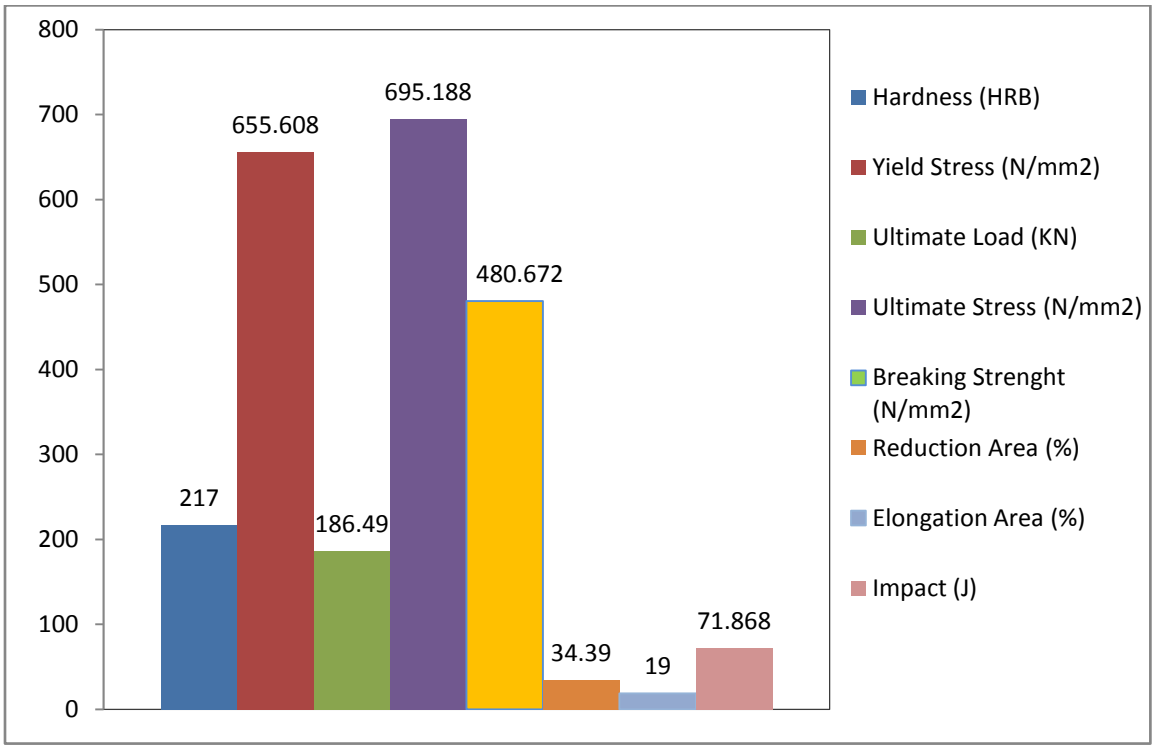


Figure 4.1: Mechanical properties of as-received Low Alloy steel

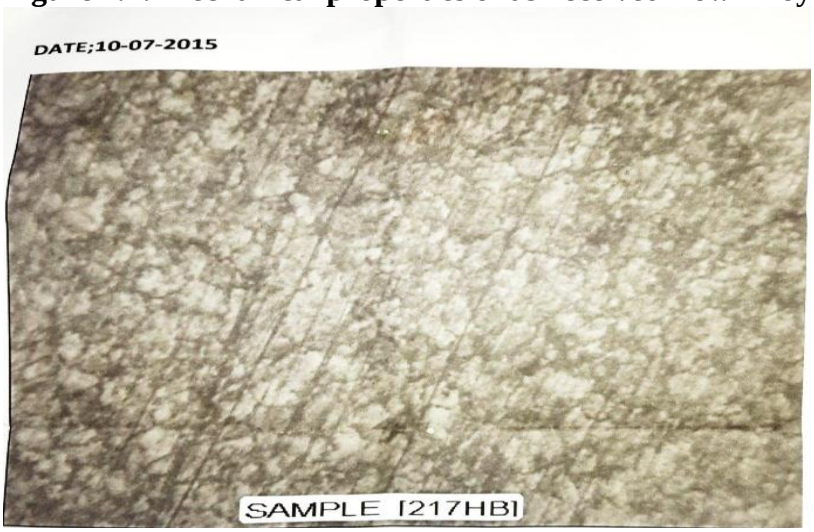


Plate 4.1: Micrograph of As-received Medium Carbon Steel (x200) showing white bands (ferrite) and dark bands (pearlite)

Figure 4.1 and Plate 4.1 presents the investigation into the mechanical propertiesand microstructure analysis of the as-received sample (medium carbon low alloy) steel. The results of the as-received steel showed that it exhibits good mechanical properties with hardness, ultimate tensile stress, and impact values of 217 HB, 695.188 N/mm^2 and 71.868 Joules respectively. Also, the micrograph (Plate 4.1) revealed that matrix of ferrite grains as white etching constituent and pearlite (a lamellar mixture of ferrite and cementite) as dark etching constituent, this indicates the microstructure of medium-carbon steel as ferritic-pearlitic microstructure appearing uniformly distributed (Pandarinathan*et al.,* 2013).

4.3 The Results of Biochemical Extraction

Table 4.2: The Percentage yield of extracts of the plants

Sample	Weight of powdered sample (g)	Weight of sample extract (g)	% yield
A	290	38.85	13.39
B	290	52.16	17.99

Table 4.2 shows the results of extraction for*Chrysophyllum albidium* and *Heliotropium indicum* leaves. A comparison of 13.39%for *Chrysophyllum albidium* to 17.99% for*Heliotropium indicum* as plants % yield of extractsindicated slight difference in the yield of extracted products whichmight be due to varied solubility of the plant in the solvents used for extraction (Mahour*et al.,* 2008)

4.4 The Results of Phytochemical Screening

Table 4.3: The results of qualitative and quantitative of phytochemicals screening of the plants extract (Sample A)

Sample	Qualitative	Quantitative (%) Composition
Alkaloid	+	0.62
Flavonoid	+	86.44
Saponin	+	16.65
Tannin	+	1.65
Steroid	-	-
Terpenoids	+	-

Key: + = Phytochemical present; - = Phytochemical absence

Table 4.4: The results of qualitative and quantitative of phytochemicals screening of the plants extract (Sample B)

Sample	Qualitative	Quantitative (%) Composition
Alkaloid	+	1.04
Flavonoid	+	96.25
Saponin	+	24.90
Tannin	+	2.05
Steroid	+	-
Terpenoids	+	-

Key: + = Phytochemical present;- = Phytochemical absence

Tables 4.3 and 4.4 show the results of the qualitative and quantitative phytochemical screening of *Chrysophyllum albidium* and *Heliotropium indicum plants* extracts. From the results obtained from investigations into the qualitative phytochemical of the plant leaves extract, which showed the presence of alkaloids, saponins, tannins, flavonoids in both extracts of *Chrysophyllum*

albidium(CA) and *Heliotropium indicum (HI)* leaves while steroids and tripenes were found present in Heliotropium indicum only,which further indicates that HI compoundswere highly soluble with greater affinity of compounds to organic solvent(ethanol) used for extraction ((Mahour et al. 2008;Hawaze*et al.* 2012).

Although, the presence of these secondary metabolites has contributed to its physiological activity and all tested extracts exhibited potent electrochemical reactive property. The obtained result is in accordance with the findings of Okoli and Okere (2010) and Jyoti and Sharma (2014).

However, the absence of tannins reported byOkoli and Okere (2010) is in contrast to the obtained CA results. Likewise, the corresponding values of phytochemical composition of leaves explored in this study revealed that there is varied quantities of phytochemical constituents, with significant differences ($p<9.82\%$) between the plant leaves. The results showed that the leaves of *Heliotropium indicum* had the highest composition of tannins, flavonoids, alkaloids and saponins. This could possibly explain the scientific basis for variation in chemical structure and biological properties, which greatly influence their inhibitive properties in different media. In support of these current findings, CA leaves was one of the plants earlier reported as good source of anti-nutrients with more tannins for antioxidant activity (Taiye and Pass, 2014).

4.5 The Results of Physicochemical properties

Table 4.5 presents the physicochemical investigations on parameters such as pH, colour, odour, density, viscosity and solubility of crude plant extracts. From the results, it can be seen that*Chrysophyllum abidium*crude extracts is slightly acidic (pH = 5.67),pale-yellow in colour with a pleasant odour and solid appearancewhile *Heliotropium indicum* is slightly acidic (pH = 6.31), Greenish brown in colour with honey odour and semi-solid appearance.

Table 4.5: Physicochemical properties of the plants extracts

Parameters	Sample A	Sample B
pH (29^oC)	5.67	6.31
Colour	Pale Yellow	Greenish Brown
Odour	Pleasant	Honey
Appearance	Solid	Semi-solid
Density (29^oC kgm^{-3})	1.14	1.08
Viscosity (29^oC mPa·s)	1504	302
Solubility (%w/v)		
a. Distilled water (29^oC)	0.51	10.32
b. Distilled water (60^oC)	1.96	11.98
c. Ethanol	5.95	9.26
d. Acetone	4.71	9.01

The densities of *Chrysophyllum albidium and Heliotropium indicum* extracts have values of 1.14 and 1.08 respectively. *Chrysophyllum albidium* has higher density value compared to Heliotropium indicum. This slight differencein density might be due to materials appearancewhich tends to affects some of its properties such as weight hence resulting in lower density.

The obtained values of the investigation into thekinematic viscosity ofthe extracts of the plant shows that *Chrysophyllum albidium*(sample A) is highly viscous with a viscosity value of 1504 mPa·s compared to 302 mPa·s recorded for *Heliotropium indicum* crude extracts, this indicates that it takes longer time for CA extracts to flow under same gravity through the calibrated spindle (orifice) of the automated digital viscometer at room temperature.

Also, from the obtained values of solubility, it is evident that the solubility of the plant extracts in distilled water increases with increase in temperature. This is an indication of the water

absorption characteristic of plant extracts as a result of increased degree of solvent-molecule interaction.However, Chrysophyllum albidium (sample A) is slightly soluble in distilled water (0.51%) but more soluble in ethanol(5.95%) and acetone (4.71%) while Heliotropium indicum (sample B) is freely soluble in distilled water (10.32%), ethanol (9.26%) and acetone (9.01%) solubility valuesat room temperature. The measured solubility of the plant extracts in various solvents can be explained as follow. As a rule, polar compounds are soluble in polar solvents while non-polar compounds are soluble in non-polar solvents. Although, water is a universal solvent, its ability to dissolve polar compounds has been strongly established and is attributed to its high dielectric constant. Ethanol and acetone are organic solvent. However, ethanol can ionize to produce hydroxyl ion (OH-). Consequently, the dielectric constant of ethanol is relatively higher than those of the other organic compounds such as acetone (Eddy *et al.*, 2014). Therefore, to some extent, ethanol is able to dissolve the plant extracts.

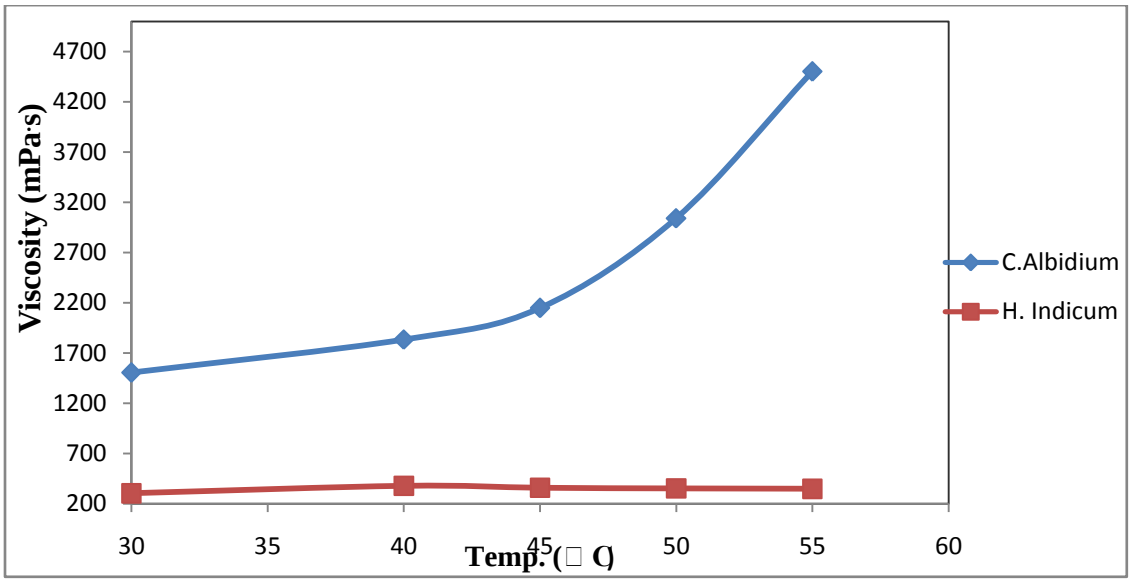


Figure 4.2: The Rheological Behaviour of the plant extracts

Fig. 4.2 shows the variation of viscosity when thermal stress varies from 40^{o}C - 55^{o}C temperatures.An important mechanical property of fluids is viscosity; rheological behaviour is basic consideration in food industry such as pasteurization, evaporation, drying and aseptic

processing. After, the rheological study of the plant crude extracts at varied temperature from 30^{o}C - 55^{o}C it was found that the extracts internal flow resistance is dependent of the external force which is acting upon the fluid changes at various temperatures as they are not ideally viscous (Fig 4. 2).

Chrysophyllum albidium crude extract showed increasing trend of viscosity from 1833 mPa·s (40^{o}C) up to 4501 mPa·s (550^{o}C) which indicates a shear- thickening behaviour while Heliotropium indicum extracts showed decreasing trend of viscosity from 377 mPa·s (40^{o}C) down to 347 mPa·s (55^{o}C) and indicates shear- thinning behaviour (Thomas, 2011). Alhough, Chrysophyllum albidium crude extract shows it ability to give structure by the formation of gel during heating and cooling without breaking the structure (Malviya*et al.,* 2010), this is of great concern to act in context of flow system, therefore there is need for improvement of its rheological properties so as to enhance the viscosity ratein order not to coagulate with fluids.

4.6 The Results of Biodegradability Test

Figure 4.3 shows the investigation into Biochemical Oxygen Demand (BOD) of tested inhibitors and their optimum formulations.From the results obtained, it is clear that BOD curves gave a general trend of decrease in oxygen level with incubation time indicating that biodegradation occurs in the formulated inhibitors.

Although, Shell Ensis SX inhibitor formulation show increase of oxygen level after a period of twenty (20) days and followed the trend up to twenty-eight (28) days which indicates that lower oxygen consumption occurred between and after twenty five (25) days. The organic corrosion inhibitor formulate has greater tendency of degradation far more than that of Shell Ensis SX

inhibitor formulation which does not show clearly duration over which it will persist in the environment.

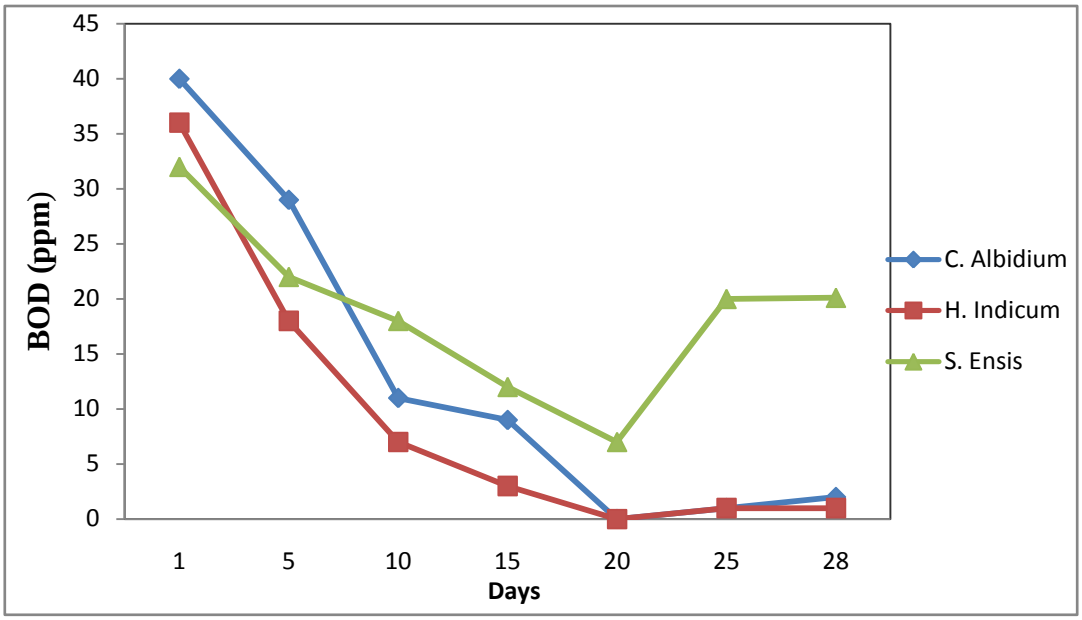


Figure 4.3: Variation of Biochemical Oxygen Demand with time (days) of inhibitors

The oxygen level at 28 days is lower in Heliotropium indicum inhibitor formulation than in Chrysophyllum albidium and Shell Ensis inhibitors formulation, the dissolved oxygen levels were found to be 1 ppm for Heliotropium indicum, while Chrysophyllum albidium and Shell Ensis SX are 2 ppm and 20 ppm at twenty eight (28) days and all produced inhibitors attained up to 95 percent biodegradation while Shell Ensis SX (standard) gave 62 percent biodegradation. The biodegradability of Heliotropium indicum and Chrysophyllum albidium extracts indicates rapid degradability results, therefore are not toxic to plant and animal, micro and macro organism but Shell Ensis SX does not show much significant environmental friendliness of the corrosion inhibitor produced from the test results. This is consistent with the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) statement that a chemical that is readily biodegradable in fresh will also be degradable in marine environments (ECETOC, 1993). However, the experimental results obtained in the present study demonstrated biodegradation of

inhibitors under laboratory conditions, although the extent of biodegradation was not further quantified.

4.7 The Results of Proximate analysis

Table 4.6: The results of the proximate analysis of the leaves of the plants

Components	Sample A (%)	Sample B (%)
Moisture	8.45	3.65
Ash	21.91	6.30
Crude lipid	17.28	30.17
Crude Protein	12.23	6.99
Crude fibre	15.4	16.95
Carbohydrate	40.13	52.89

Table 4.6 shows the results of the proximate analysis of *Chrysophyllum albidium* and *Heliotropium indicum* leaves employed in this study. The results shows that *Chrysophyllum albidium* contains crude fibre (15.4%), crude protein(12.23%), ash(21.91%), carbohydrate (40.13%), moisture (8.45%) and crude fat (17.28%) while *Heliotropium indicum contains* crude fibre (16.95%),crude protein(6.99%), ash(6.30%), carbohydrate (52.89%), moisture (3.65%) and crude fat (30.17%).

From the result obtained, moisture has the least value, while carbohydrate has the highest value. Also, *Chrysophyllum albidium* leaves has the highest amount of protein, moisture and ash content while *Heliotropium indicum has* the highest amount of carbohydrate, fibre, and fats this is an evident that varied levels of anti-nutrients are present in each plant leaves. Although, The high ash content of *Chrysophyllum albidium* indicates that the leaves are rich in mineral elements while the low moisture content in *Heliotropium indicum* would hinder the growth of

microorganism and promotes storage life. The tested plants contained food parameters that support better utilization in domestic industries and bioactive components responsible for inhibitive activity (Adeyeye and Ayejuyo, 1994).

4.8 The Results of FTIR Analysis

The frequencies and peaks of the IR adsorption deduced from the FTIR spectra of plants extract and the corrosion productproduced in the presence of inhibitor are presented in Figures 4.4 – 4.7.

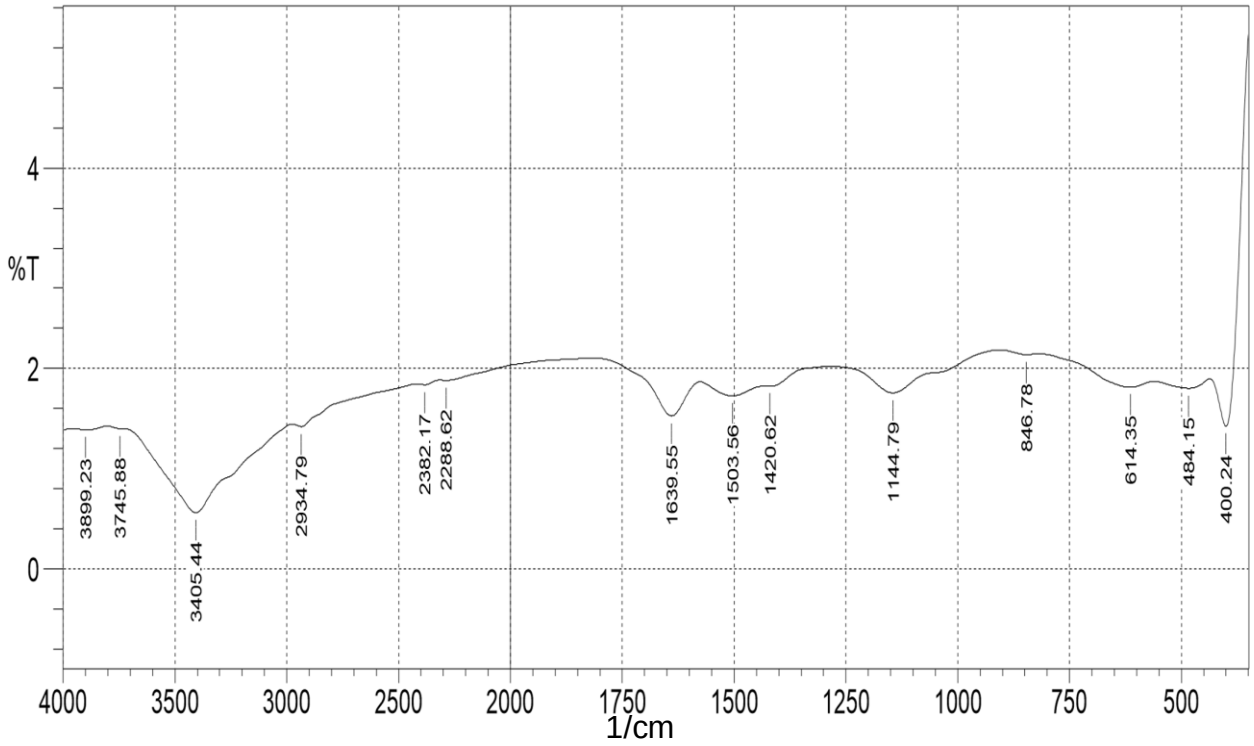


Figure 4.4: The IR spectrum of sample A

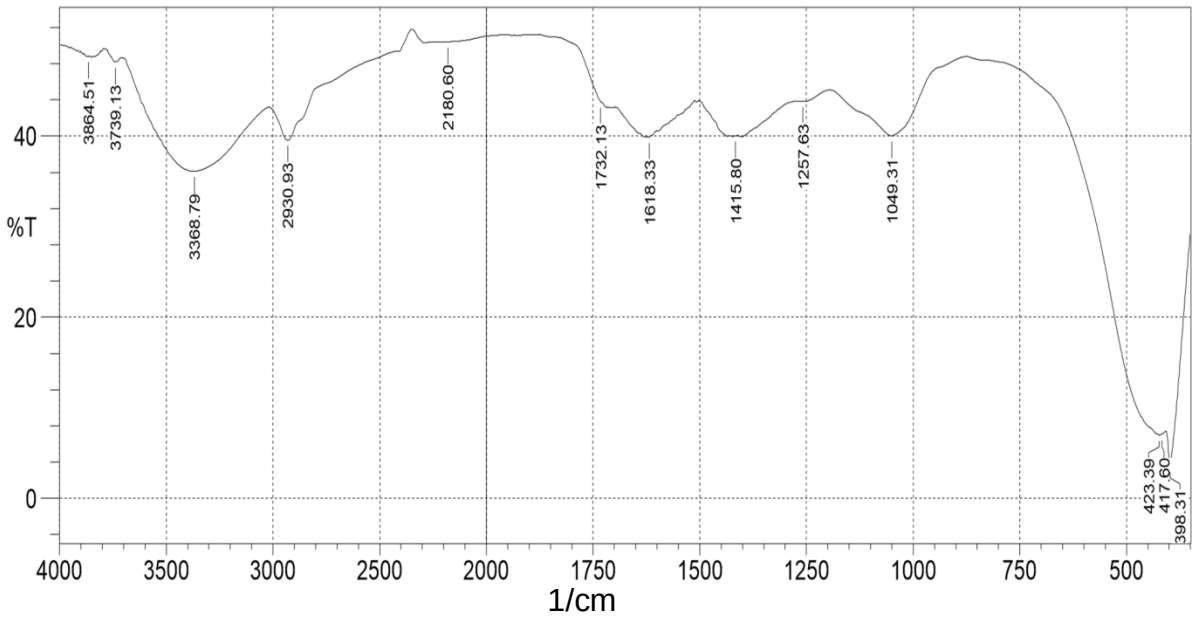


Figure 4.5: The IR spectrum of sample B

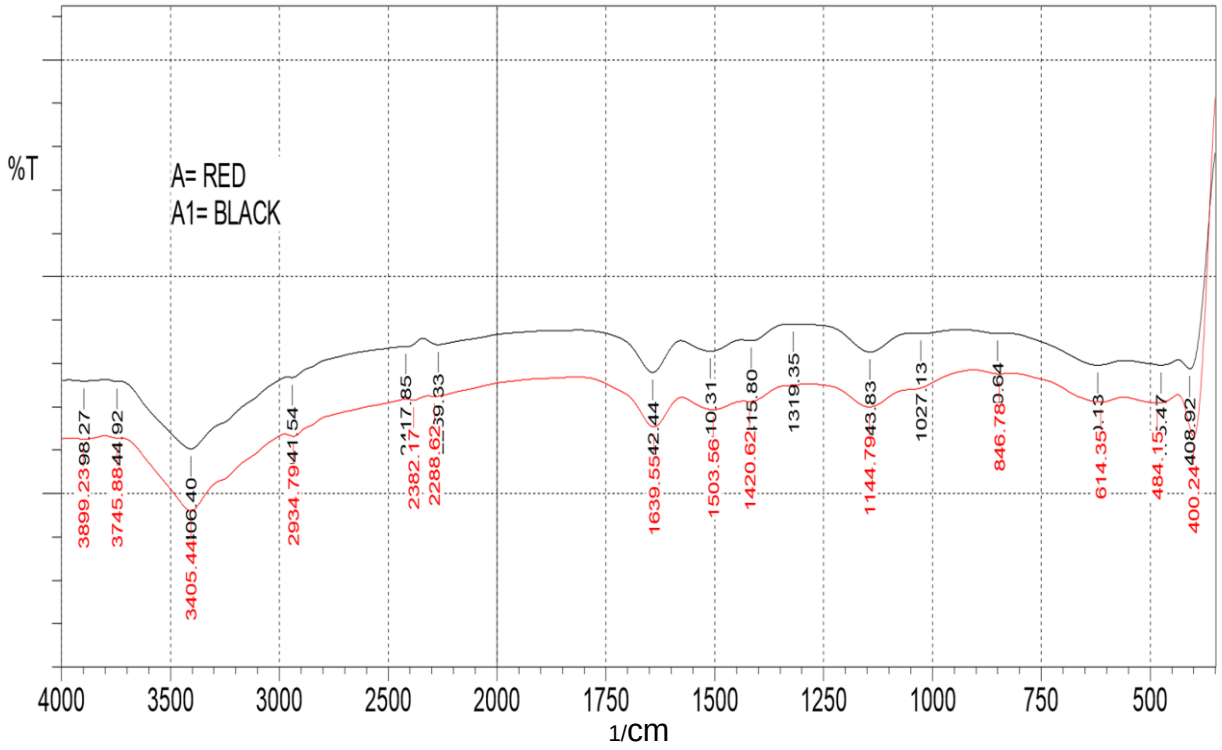


Figure 4.6: The IR spectrum of sample A (red) and protective film (black)

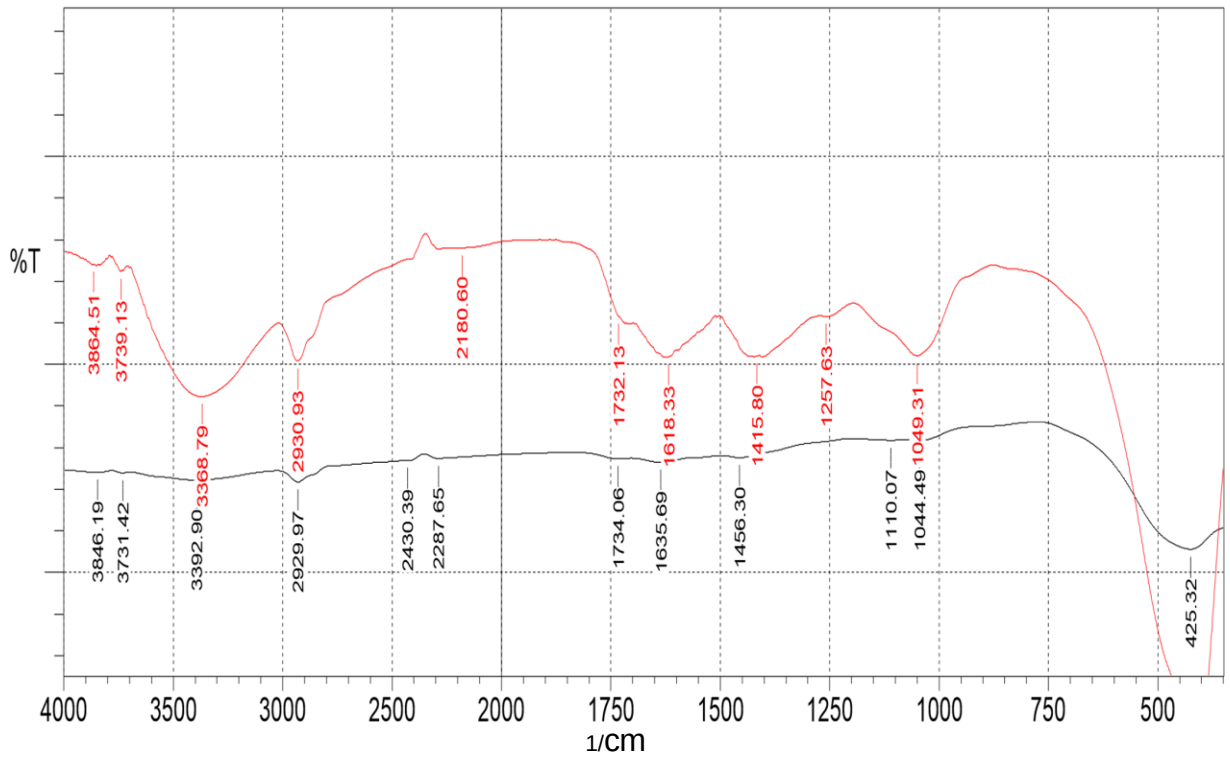


Figure 4.7: The IR spectrum of sample B (red) and protective film (black)

From the results obtained, it is observed that the FTIR spectrum of *Chrysophyllum albidium* indicated the presence of four functional groups, notably, the C=O stretch at 2288.62 cm^{-1}, C=C bends at 2382 cm^{-1}, the C≡C stretch at 2934.79 cm^{-1}, and the OH stretches at 3405.44 cm^{-1}, 37545.88 cm^{-1} and 3889.23 cm^{-1}, while the FTIR spectrum of *Heliotropium indicum* indicated the presence of some functional groups, notably, the C=O stretches at 2180.60 cm^{-1}, C-H aliphatic stretch at 2930.93 cm^{-1}, and the OH stretches at 3368.79 cm^{-1}, 3739.13 cm^{-1} and 3864.51 cm^{-1}, respectively. A comparison of the spectrum of *Chrysophyllum albidium* and *Heliotropium indicum* crude extracts indicated that they contained different function groups.

Figures 4.6 - 4.7 reveals the FTIR spectrum of the protective film formed on the surface of the metal after immersion in the HCl solution containing 500ppm of*Chrysophyllum albidium (CA)* and *Heliotropium indicum (HI).* A comparison of the notable spectrum of *CA* crude extracts and that of the corrosion product after the extracts has been used as inhibitor indicated that the C=O

stretch at 2288.62 $cm^{-1}$is shifted to 2239.33 cm^{-1}, C=C bends at 2382 cm^{-1} is shifted to 2417.85 cm^{-1}, the C≡C stretch at 2934.79 cm^{-1} is shifted to 2941.54 cm^{-1}, and the OH stretches at 3405.44 cm^{-1}, 3745.88 cm^{-1} and 3889.23 cm^{-1} are shifted to 3406.40 cm^{-1}, 3744.92 cm^{-1} and 3898.27 cm^{-1} while *HI* indicated that the C=O stretches at 2180.60 cm^{-1} is shifted to 2287.65 cm^{-1}, C-H aliphatic stretch at 2930.93 cm^{-1} is shifted to 2929.97 cm^{-1}, and the OH stretches at 3368.79 cm^{-1}, 3739.13 cm^{-1} and 3864.51 $cm^{-1}$are shifted to 3392.90 cm^{-1}, 3731.42 cm^{-1} and 3846.19 cm^{-1},among others respectively. These shifts in frequencies suggest the existence of an interaction between the inhibitor and steel surface. Also, new functional groups were found in the spectrum of *Chrysophyllum albidium (CA)*and *Heliotropium indicum (HI)*protective films. These included, the C-Ostretch at 1319.35 cm^{-1} and C-N stretch at 1027.13 $cm^{-1}$for CA and C=C stretches at 2430.39 $cm^{-1}$for HI (Eddy *et al.*, 2014)

4.9 Corrosion Tests

Corrosion tests were conducted usinggravimetric based mass loss and LPRmethods**.** The effects of concentration from 100 - 500ppm of tested inhibitors and temperature range from 30^{o}C - 60^{o}C on Inhibition Efficiency (I.E.) was investigated and applied to different isothermal equations.

4.9.1 Weight Loss Method

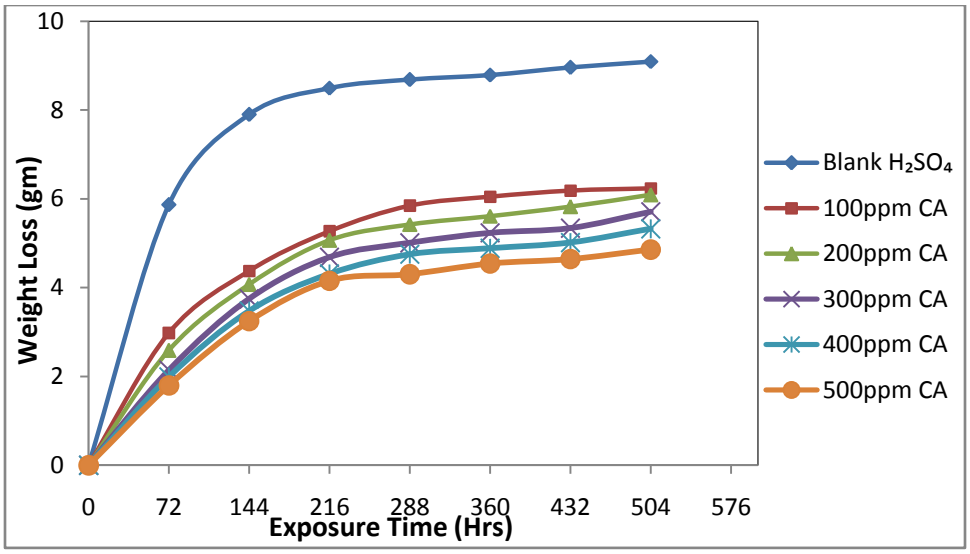


Fig. 4.8: Variation of weight loss of steel sample with time in 1M H_2SO_4 solution in the presence of formulated inhibitors of *Chrysophyllum albidium* (CA) inhibitor.

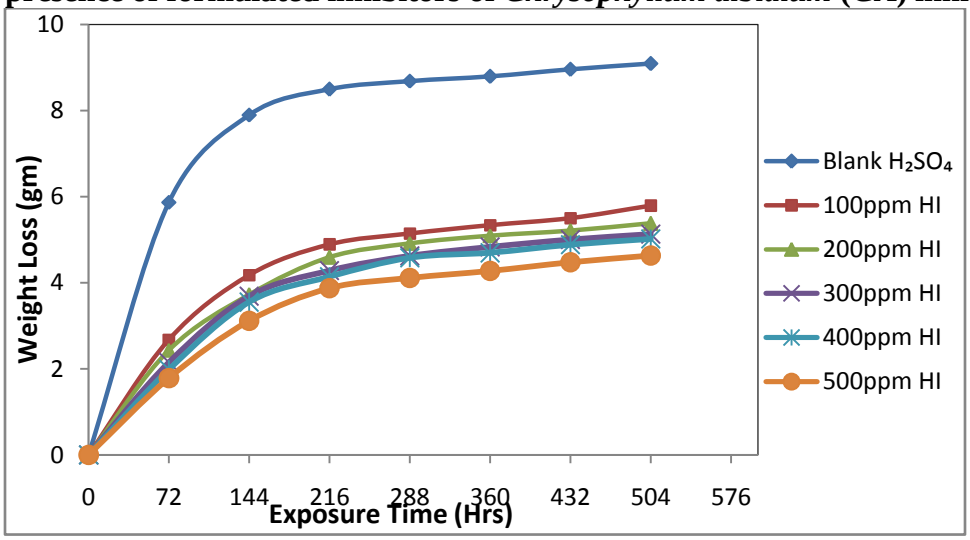


Fig. 4.9: Variation of weight loss of steel sample with time in 1M H_2SO_4 solution in the presence of formulated inhibitors of *Heliotropium Indicum* (HI) inhibitor.

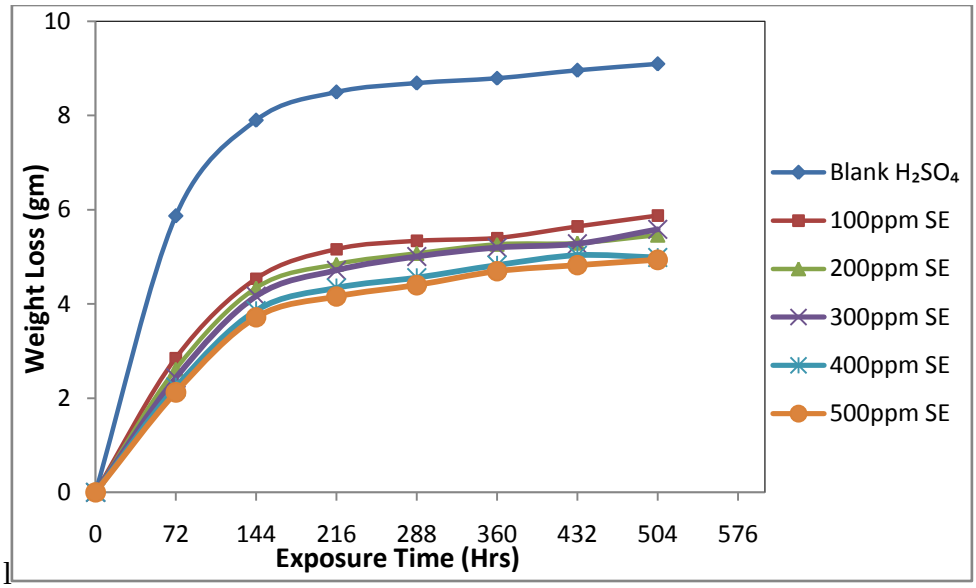


Fig. 4.10: Variation of weight loss of steel samplewith time in 1M H_2SO_4 solution in concentration 0f the standard inhibitor (Shell Ensis; SE).

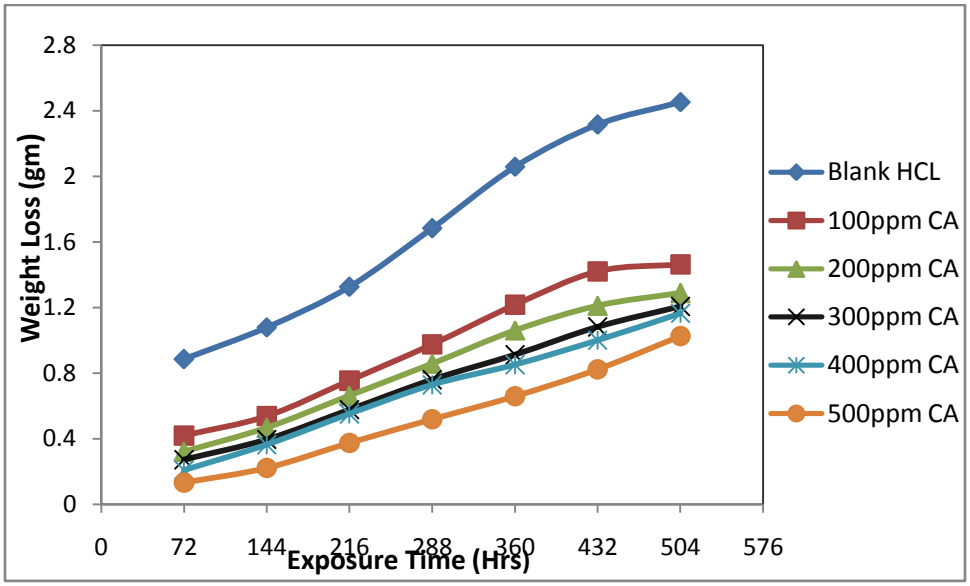


Fig. 4.11: Variation of weight loss of steel sample with time in 1M HCl solution in the presence of formulated inhibitors of *Chrysophyllum albidium* (CA) inhibitor.

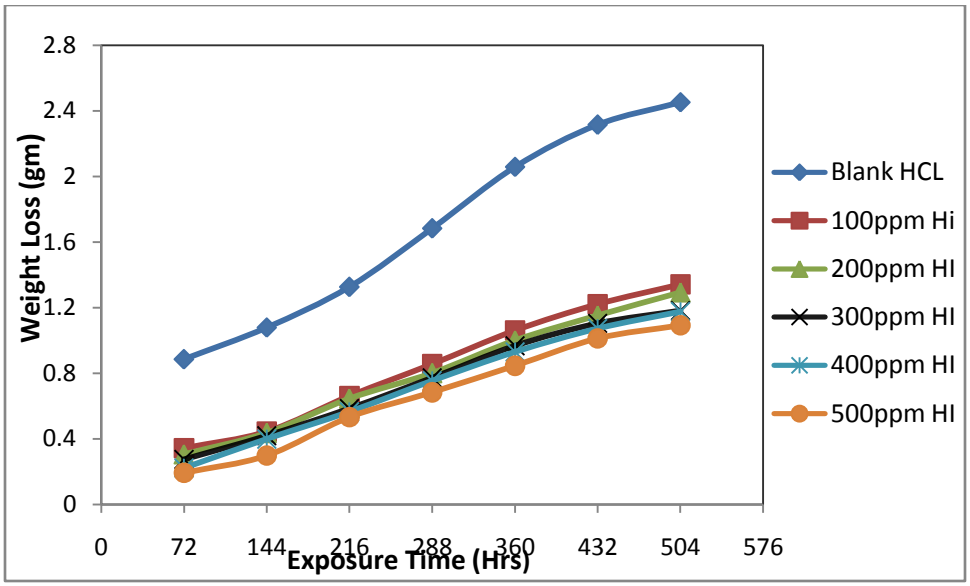


Fig. 4.12: Variation of weight loss of steel sample with time in 1M H_2SO_4 solution in the presence of formulated inhibitors of *Heliotropium Indicum* (HI) inhibitor.

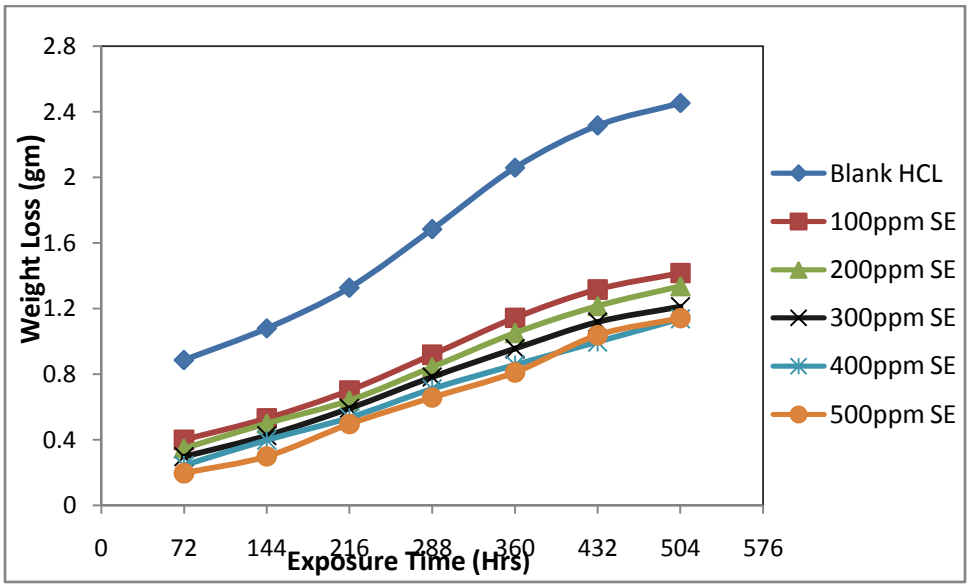


Fig. 4.13: Variation of weight loss of steel sample with time in 1M HClsolution in concentration 0f the standard inhibitor (Shell Ensis; SE).

Figures 4.8 – 4.13 show the variation in weight loss of test specimen in 1M H_2SO_4 and HCl solutions in the presence and absence of varying concentration of the formulated inhibitors as a function of time. The concentration of the inhibitors was varied from 100ppm to 500ppm, and the time of immersion was varied from 72 hours to 504 hours at room temperature. From the results obtained it was observed that weight-loss increase with increase in immersion time but decrease with increase in concentration of the formulated inhibitors. The increase in concentration of the inhibitors resulted in increased in the surface coverage on the metal and the adsorption of some inhibitor constituents on the metal surface thereby creating a barrier between the metal and the acidic medium. This enhances the inhibition of the metal and resulted to small amount of weight loss with respect to the uninhibited metal. Also, it was noticed that the inhibition strength depends directly on the concentration of inhibitors. This is in good agreement with the works of Yawas (2005) and Yaro *et al.* (2010).

In comparison, the addition of inhibitors to the corrosive media resulted in a significant reduction in theweight loss of thetest samples in comparison with the blank solution. The inhibitor formulated fromH_2SO_4 solution could not reduce the weight loss considerably as that of inhibitors from HCl solution. This could be probably due to the anions of acids Cl− dissociate physically on the positively charged metal surface, giving rise to a negative charge on the metal surface before the organic cations are physically attracted to the anions layer which formed protective films on the metal surface due to the smallest anion (Cl−) attracted faster than the biggest one (SO_4^-) on to the metal surface leading to good inhibitor performance in HCl.This is in agreement with findings of Amin *et al*. (2009) and Ehteram (2007).

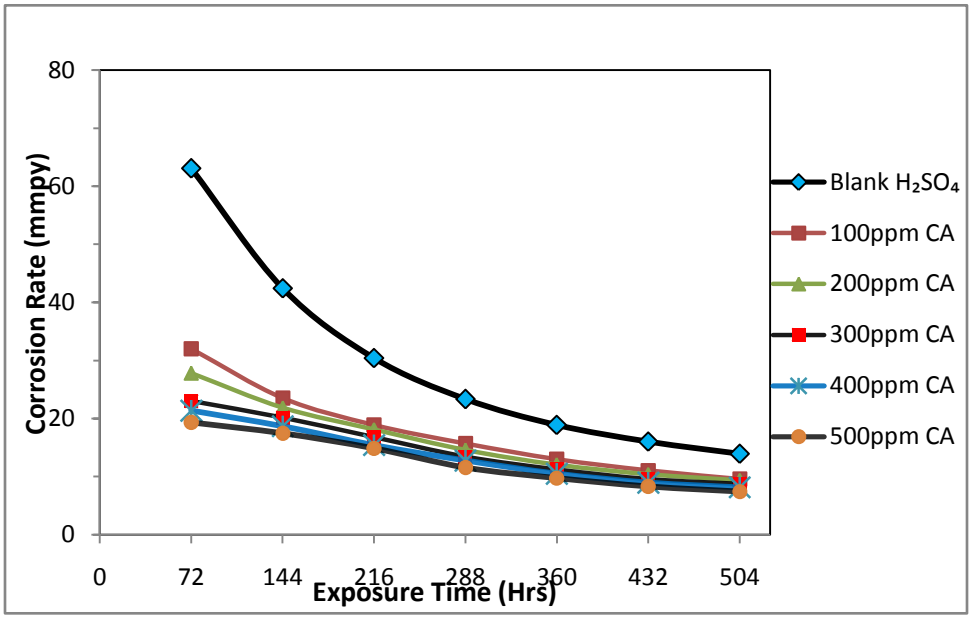


Fig. 4.14: Variation of corrosion rate of steel sample with time in 1M H_2SO_4 solution in the presence of formulated inhibitors of *Chrysophyllum albidium* (CA) inhibitor

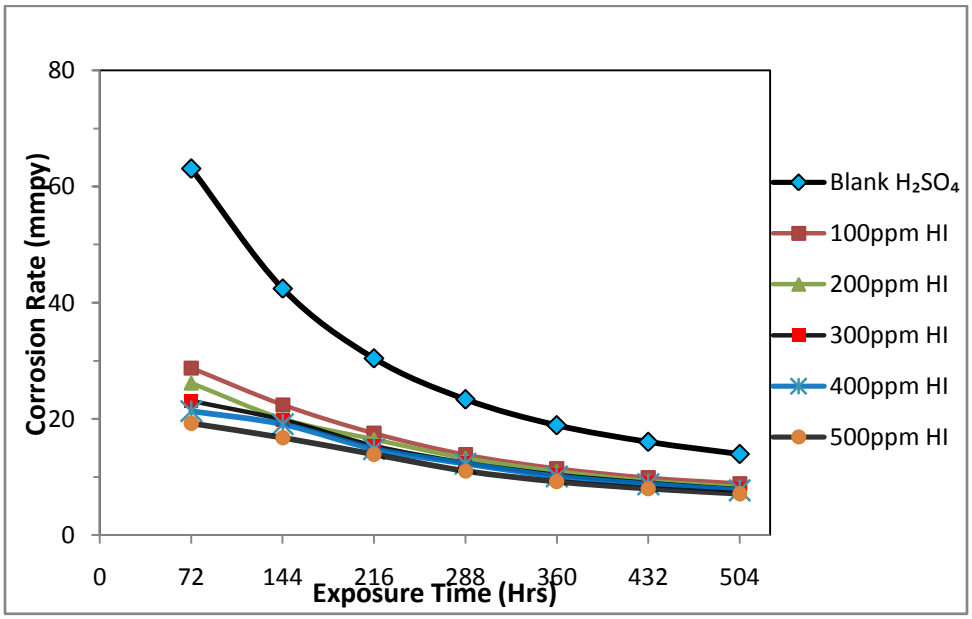


Fig. 4.15: Variation of corrosion rate of steel sample with time in 1M H_2SO_4 solution in the presence of formulated inhibitors of *Heliotropium Indicum* (HI) inhibitor

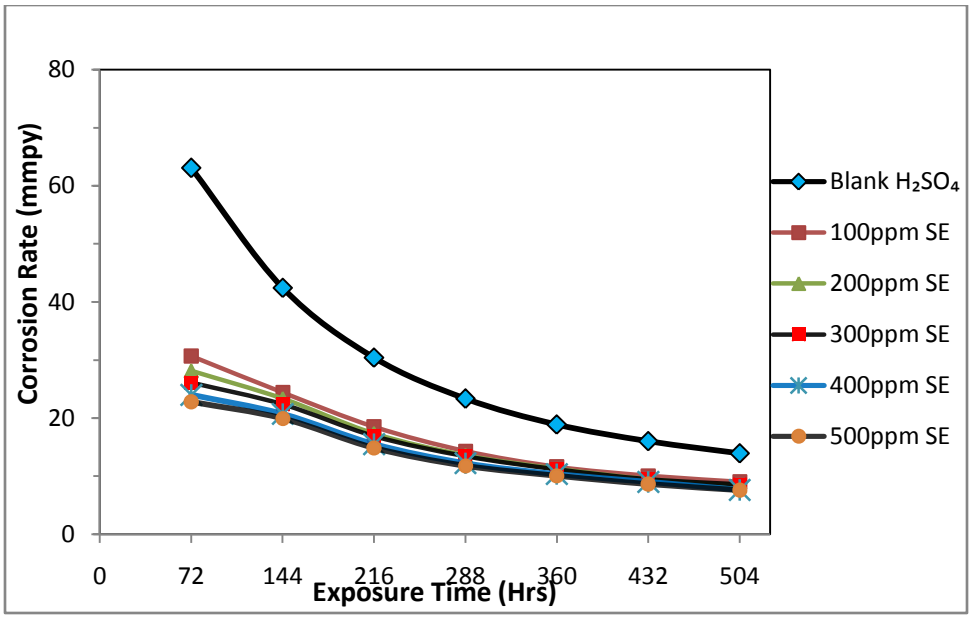


Fig. 4.16: Variation of corrosion rate of steel sample with time in 1M H_2SOsolution in concentration of the standard inhibitor (Shell Ensis; SE).

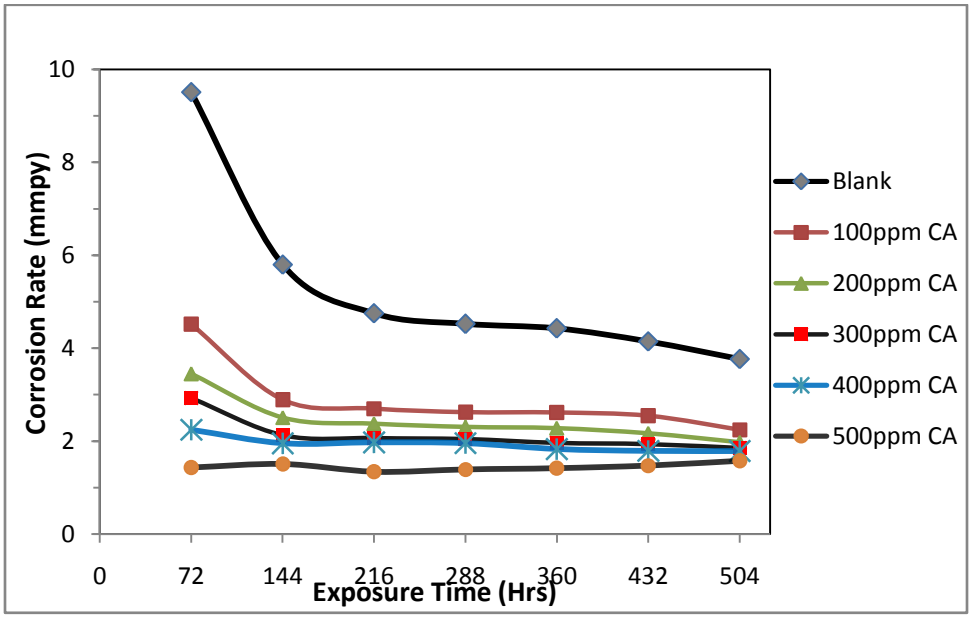


Fig. 4.17: Variation of corrosion rate of steel sample with time in 1M HClsolution in the presence of formulated inhibitors of *Chrysophyllum albidium* (CA) inhibitor.

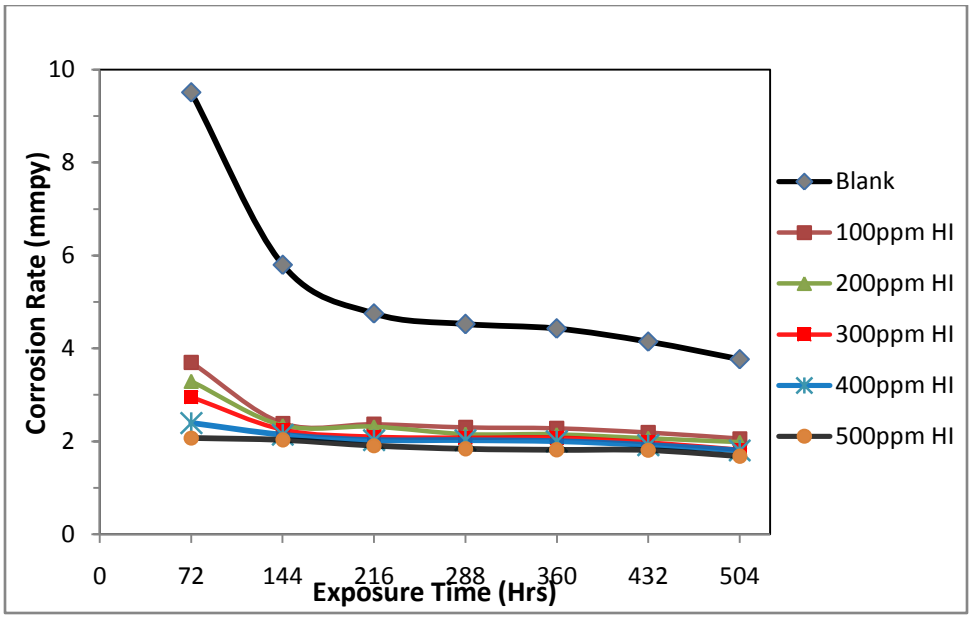


Fig. 4.18: Variation of corrosion rate of steel sample with time in 1M HClsolution in the presence of formulated inhibitors of *Heliotropium Indicum* (HI) inhibitor.

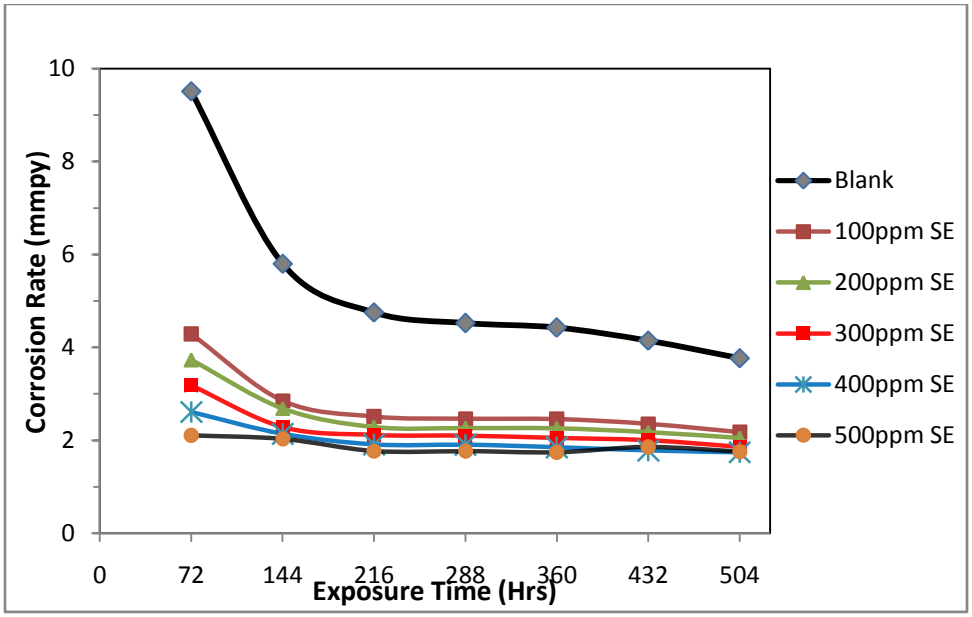


Fig. 4.19: Variation of corrosion rate of steel sample with time in 1M HClsolution in concentration of the standard inhibitor (Shell Ensis; SE).

Figures 4.14 – 4.19 shows the variation in corrosion rate of steel sample in 1M H_2SO_4 and HCl solutions in the presence and absence of different concentration of the formulated inhibitors as a function of immersion time. From the results, It is noticed that the presence of inhibitors does not stop the corrosion completely, but rather inhibits the corrosion process by reducing the corrosion rate to a minimal controllable level.

The decrease in corrosion rate of blank solution with time is a direct result of passivity, which then deters further corrosion from occurring. In comparison(Fig. 4.14 – 4.19), the corrosion rate of the medium carbon alloy steel has relatively high value of 63 $mmpy^{-1}$in 1.0 M H_2SO_4 than9.52 $mmpy^{-1}$ in 1.0 M HCl solution, meaning corrosion rates was more pronounced in uninhibited H_2SO4 solution, and then corrosion rates of the medium carbon low alloy steel significantly decreased with the presence of various inhibitors in the corrosive medium up to the values of 1.43 $mmpy^{-1}$, 2.08 $mmpy^{-1}$ and 2.12 $mmpy^{-1}$ for *Chrysophyllum albidium*, *Heliotropium indicum* and Shell Ensis respectively at immersion time of 72 hour with a further decreased of1.68 $mmpy^{-1}$ and 1.75 $mmpy^{-1}$ for *Heliotropium indicum* and Shell Ensis after immersion time of 504 hours in HCl medium. In contrast, due to the moderate corrosion resistance of the investigated medium carbon low alloy steel and aggressive blank solution of 1.0 M $H_2SO_4$and HClbecame weaker with increased exposure time, the corrosion inhibiting effect of all the tested inhibitors became weaker by increasing the immersion time. In most cases the corrosion rate of coupons decrease with the increase of the immersion time which confirmed that the inhibitors effectively protects the steel samplesup to 504 hours and in good agreements with weight loss measurements.

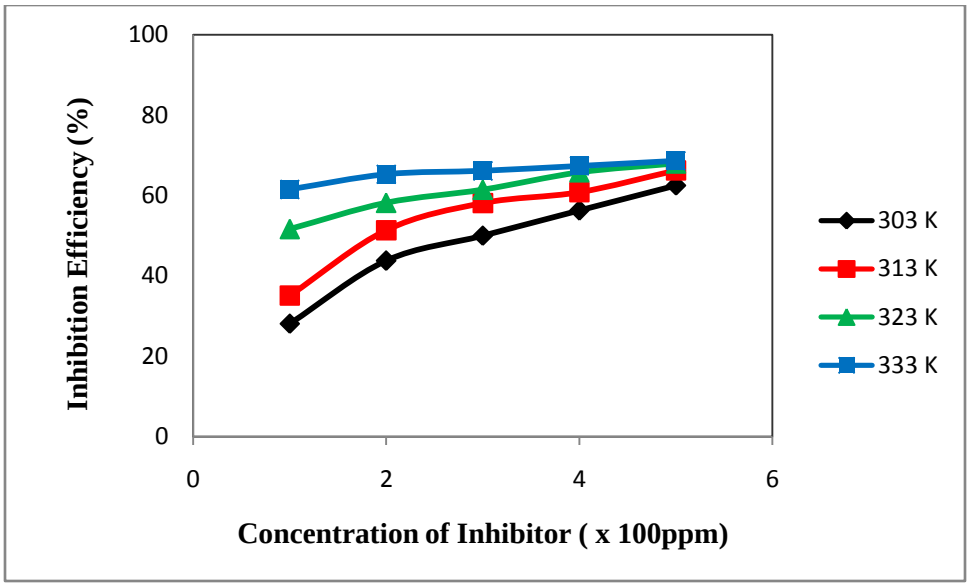


Fig. 4.20: Variation of inhibition efficiency of *Chrysophyllum albidium* (CA) inhibitor with temperature in 1M H_2SO_4 solution.

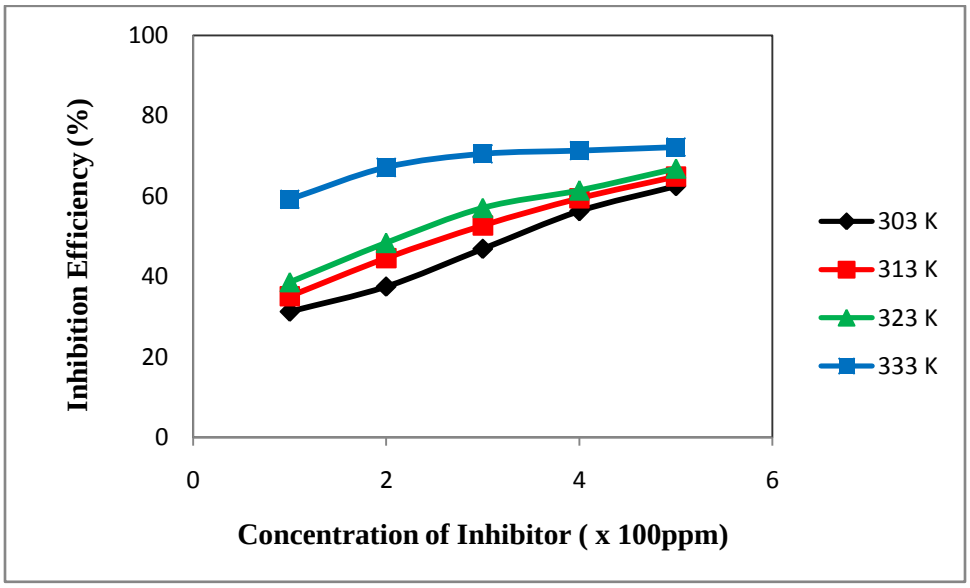


Fig. 4.21: Variation of inhibition efficiency of *Heliotropium Indicum* (HI) inhibitor with temperature in 1M H_2SO_4 solution.

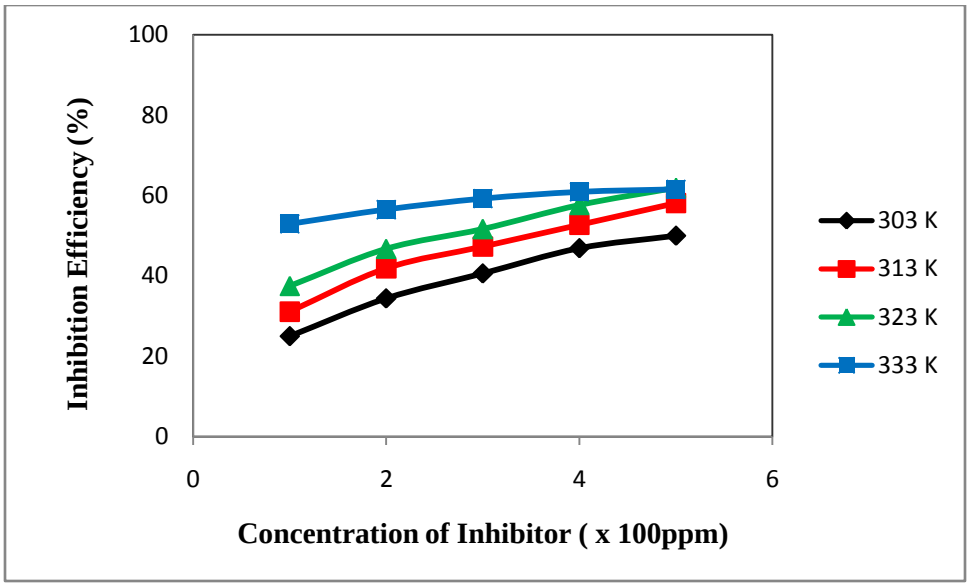


Fig. 4.22: Variation of inhibition efficiency of *Shell Ensis* (SE) inhibitor with temperature in 1M H_2SO_4 solution.

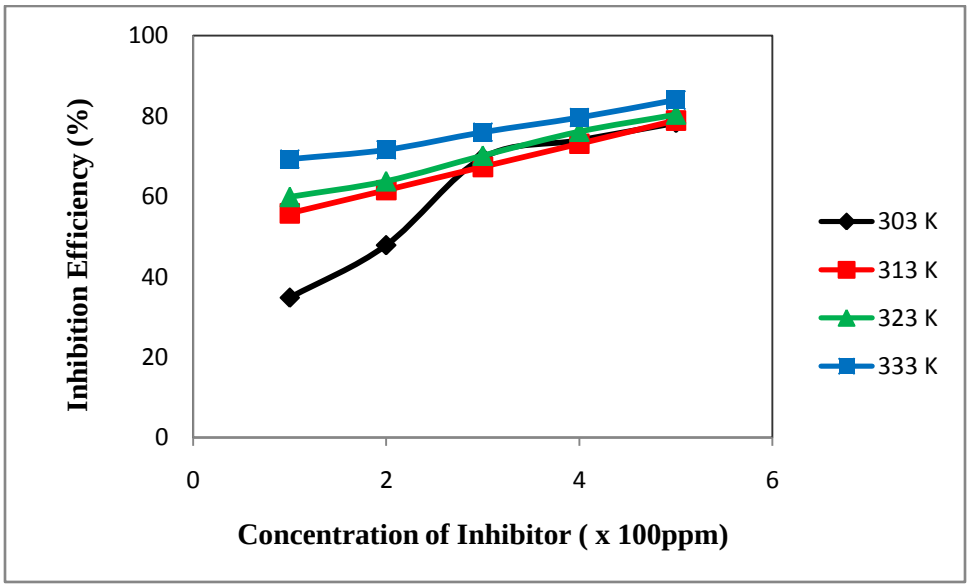


Fig. 4.23: Variation of inhibition efficiency of *Chrysophyllum albidium* (CA) inhibitor with temperature in 1M HCl solution.

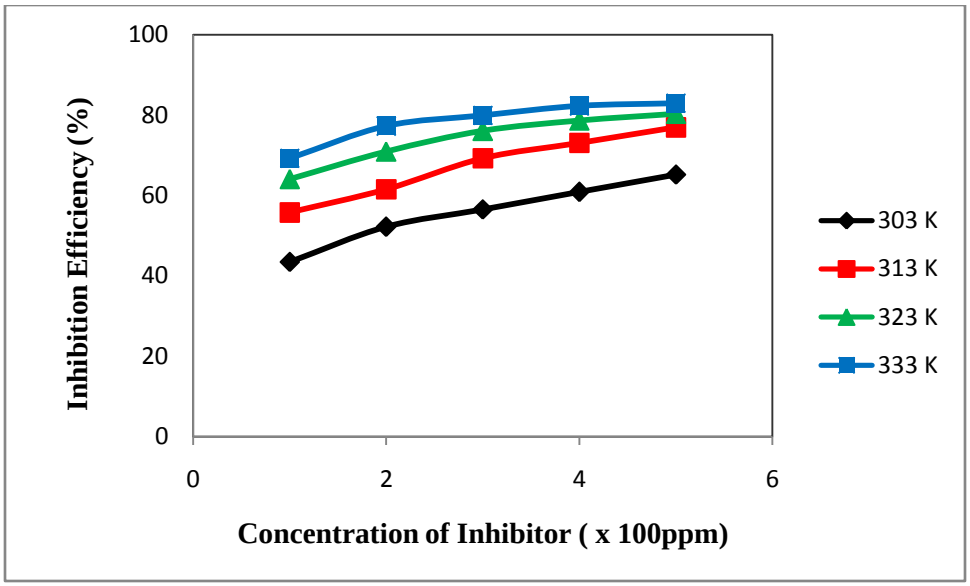


Fig. 4.24: Variation of inhibition efficiency of *Heliotropium Indicum (*HI) inhibitor with temperature in 1M HCl solution.

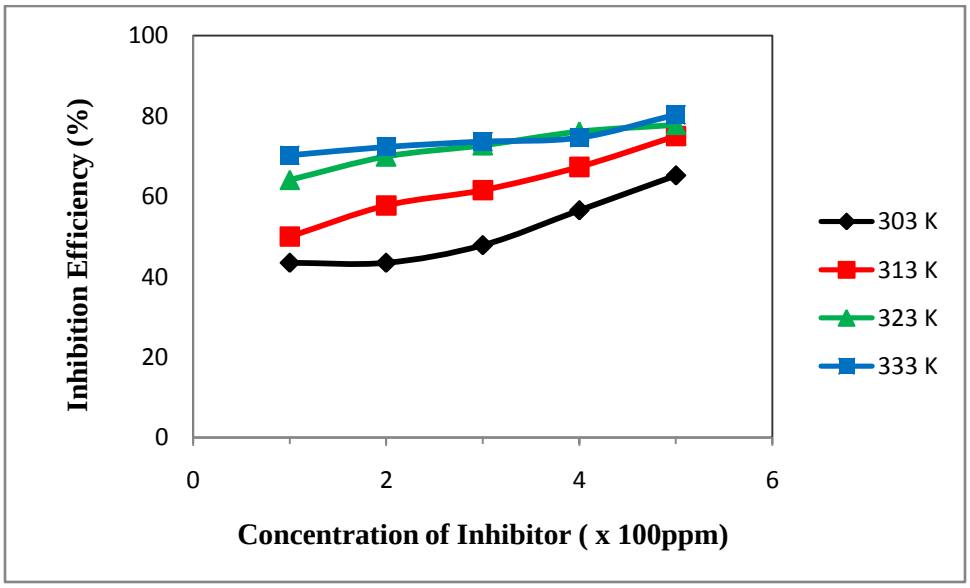


Fig. 4.25: Variation of inhibition efficiency of *Shell Ensis* (SE) inhibitor with temperature in 1M HCl solution.

The inhibiting properties of the formulated inhibitors in 1 M HCl and 1M H2SO4 was investigated in the temperature range, 303K-333K, for an hour (1) of immersion and the results are presented in Figures 4.20 - 4.25 .It indicated that, as the temperature increases from 303K to 333K, the Inhibition Efficiency (IE) also increased. The inhibitors shows good pickling inhibitors qualities as the studies compounds retain their protective properties at relatively high temperature(333K) in acidic media.The increase in IE was from 78.3 % to 84.0% for CA, 65.2 % to 82.9 % for HI and 65.2 % to 80.3 % for SE at concentration of 500ppm of studied inhibitors in 1M HCl solution. This trend was in good agreement with Ebenso observation's (Ebenso, 2003a; 2004) and findings by Aejitha*et al.* (2015) andKarthik*et al.* (2015).

The addition of inhibitors lowered the corrosion rate to the minimal level, with the inhibition efficiency increasing with increase in temperature. This may be due to the fact that physisorption is favoured at lower temperature, whereas chemisorption at higher temperature (Ebenso *et al*., 2008). Hence, the slight variation in inhibition efficiency inHCl and H_2SO_4 ranged between 52.9 % - 72.2 at 333K, this is a further evident that Cl^- ions first absorbed on steel surface in HCl solutions is quite clear (Amin *et al.*, 2009).

Although, the increased in inhibition efficiency at higher temperature could be attributed to enhance bonding interaction between the inhibitor molecules and metal surface. Generally, from the data, it can be inferred that the protective layer formed on coupons surface is due to strong adsorption of inhibitor constituents that was stable up to 333K of temperature as a result of increase temperature which further enhances the surface coverage of acidic-molecules interaction.

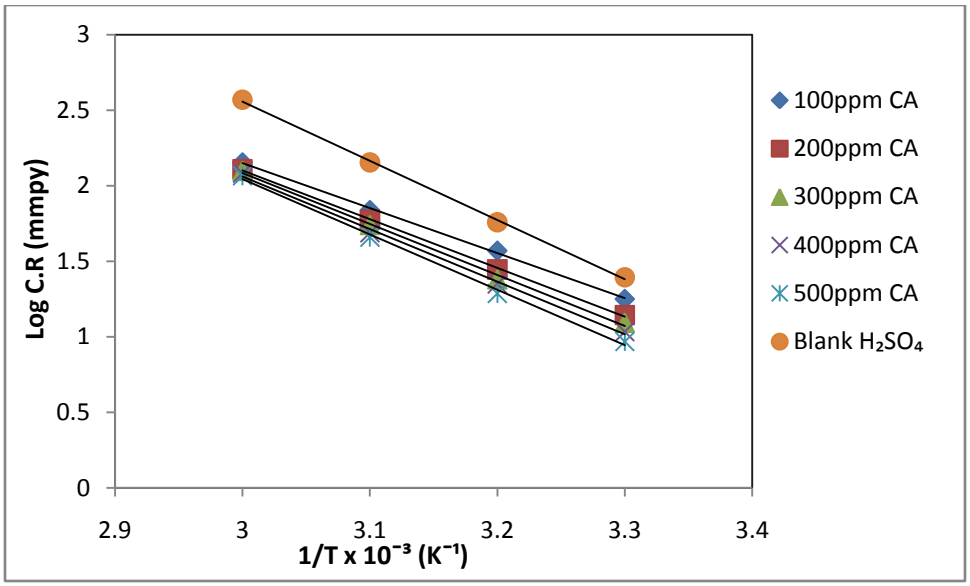


Fig. 4.26: Arrhenius plot for steel in 1M H_2SO_4 in the absence and presence of *Chrysophyllum albidium* (CA) inhibitor.

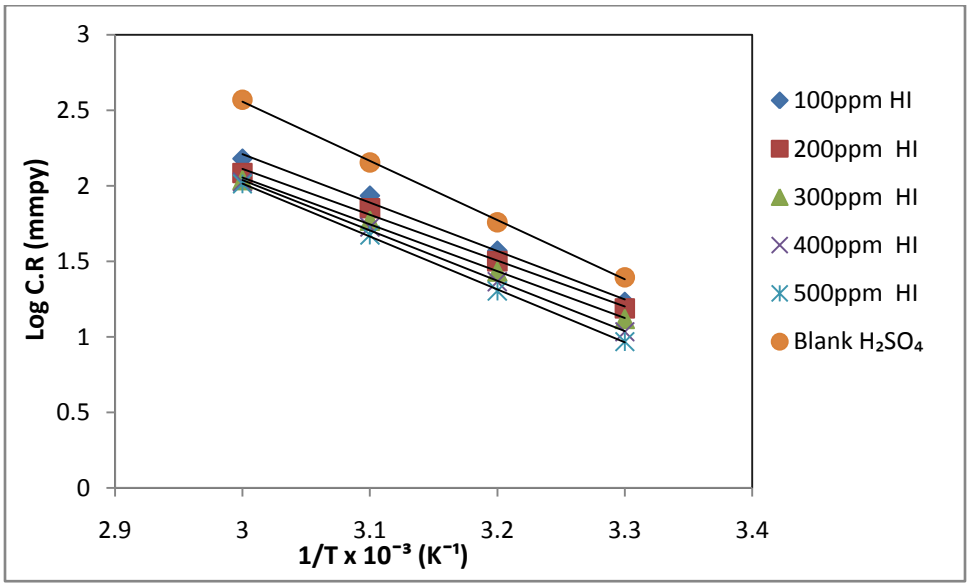


Fig. 4.27: Arrhenius plot for steel in 1M H_2SO_4 in the absence and presence of *Heliotropium indicum* (HI) inhibitor.

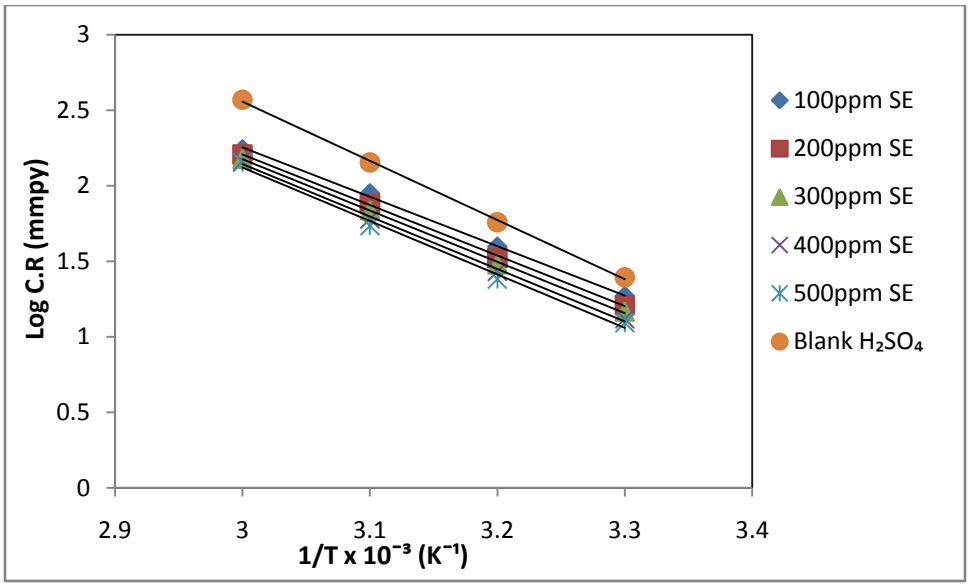


Fig. 4.28: Arrhenius plot for steel in 1M H_2SO_4 in the absence and presence of Shell *Ensis* (SE) inhibitor.

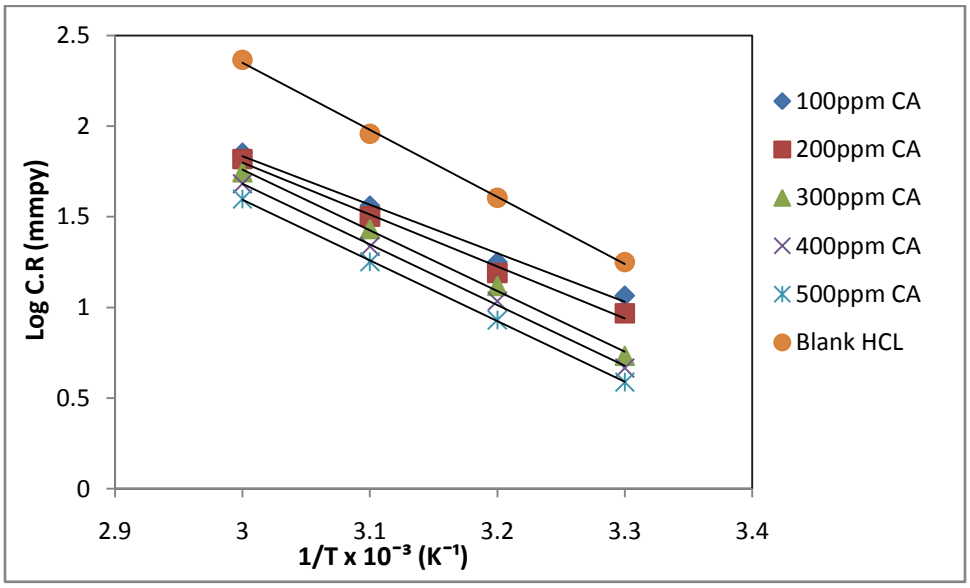


Fig. 4.29: Arrhenius plot for steel in 1M HCL in the absence and presence of *Chrysophyllum albidium* (CA) inhibitor.

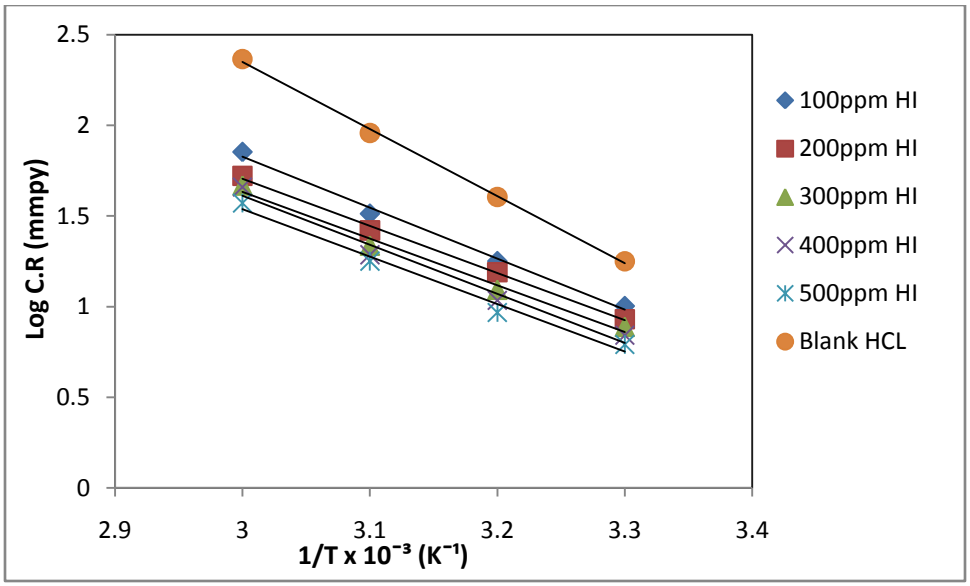


Fig. 4.30: Arrhenius plot for steel in 1M HCL in the absence and presence of *Heliotropium indicum* (HI) inhibitor.

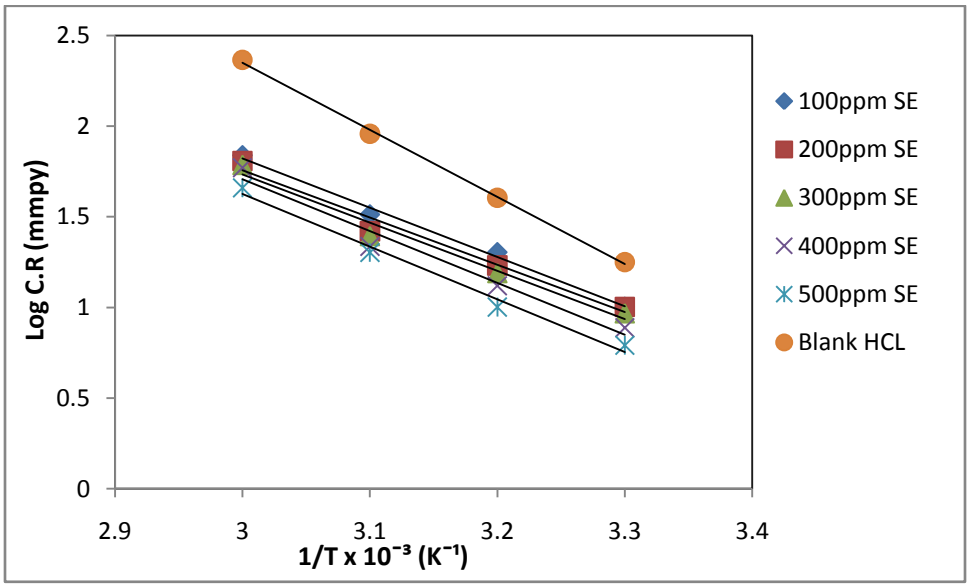


Fig. 4.31: Arrhenius plot for medium carbon low alloy steel in 1M HCL in the absence and presence of *Shell Ensis* (SE) inhibitor.

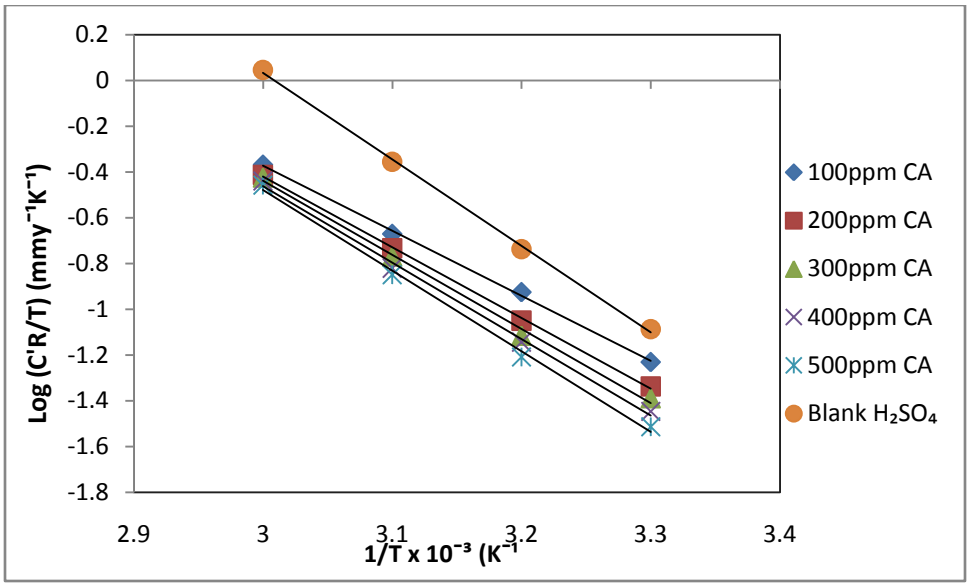


Fig. 4.32: Plot of log (CR/T) versus 1/T for medium carbon low alloy steel in 1M H_2SO_4 in the absence and presence of *Chrysophyllum albidium* (CA) inhibitor

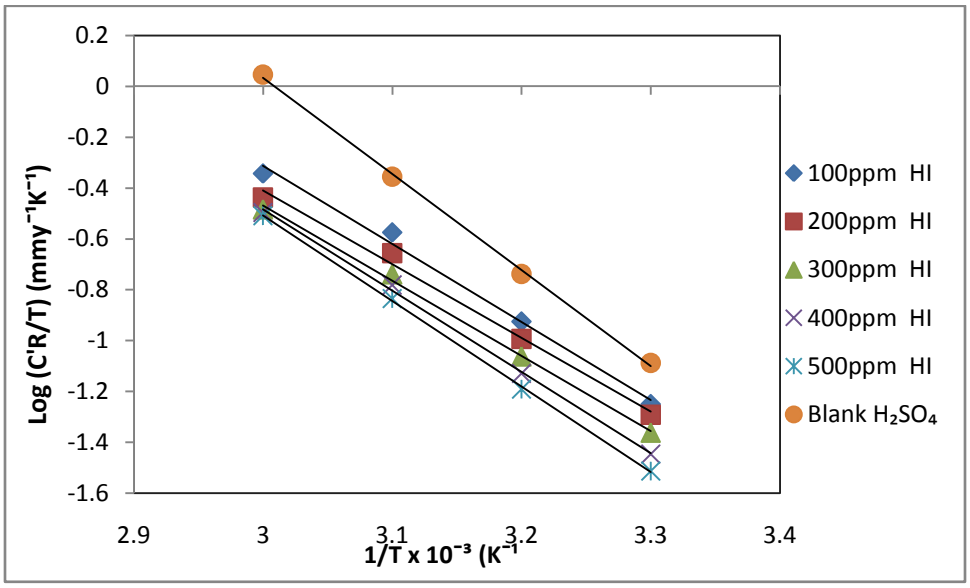


Fig. 4.33: Plot of log (CR/T) versus 1/T for medium carbon low alloy steel in 1M H_2SO_4 in the absence and presence of Heliotropium *indicum* (HI) inhibitor

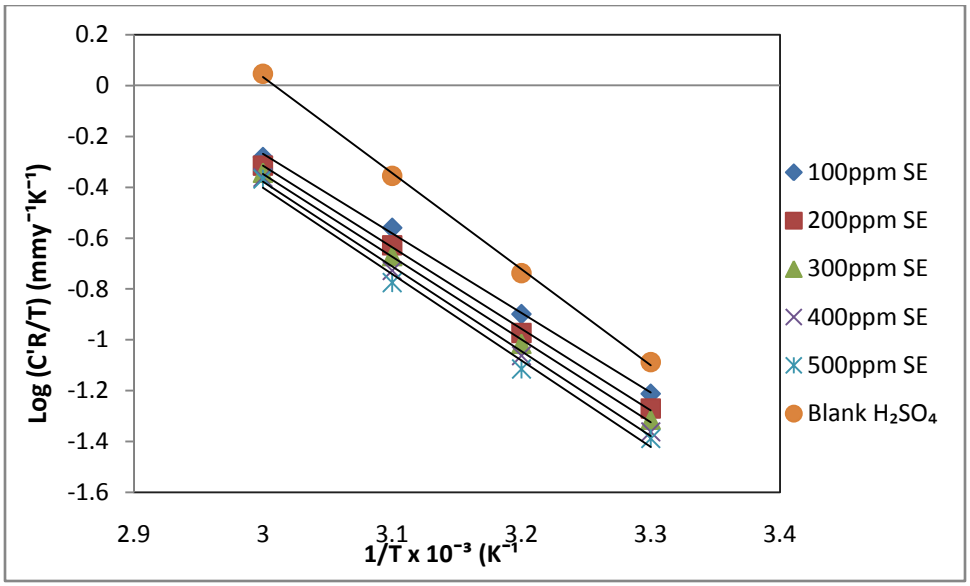


Fig. 4.34: Plot of log (CR/T) versus 1/T for medium carbon low alloy steel in 1M H_2SO_4 in the absence and presence of *Shell Ensis* (SE) inhibitor

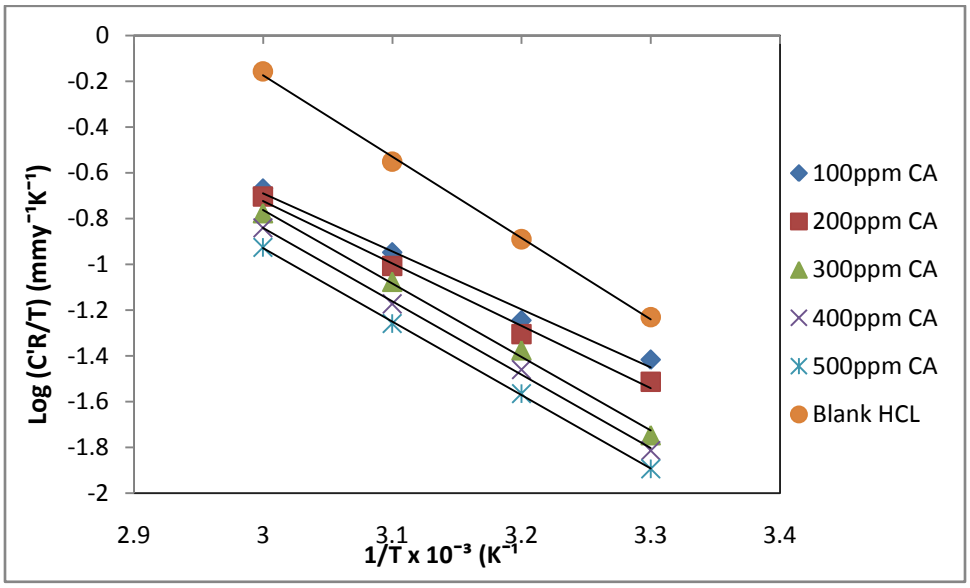


Fig. 4.35: Plot of log (CR/T) versus 1/T for medium carbon low alloy steel in 1M HCl in the absence and presence of *Chrysophyllum albidium* (CA) inhibitor

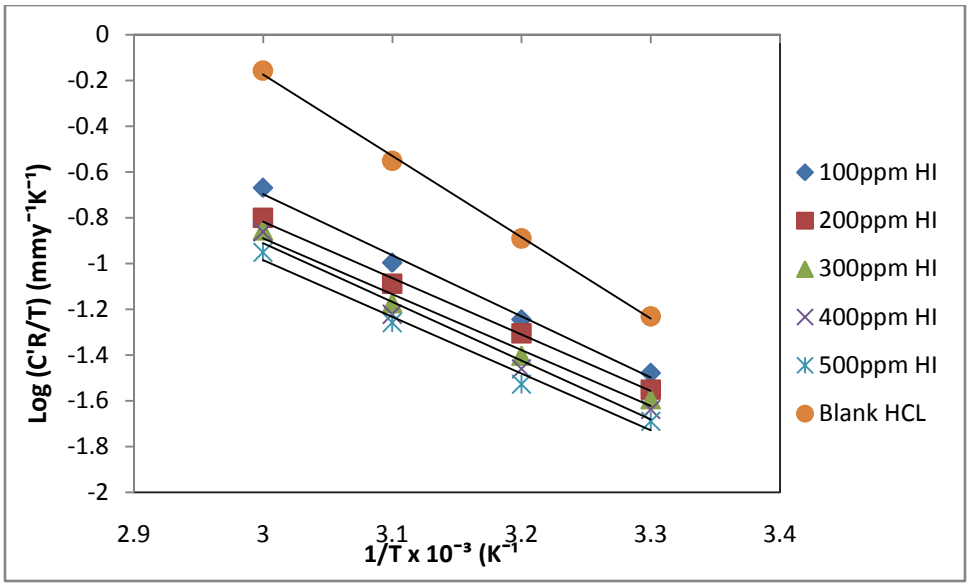


Fig. 4.36: Plot of log (CR/T) versus 1/T for medium carbon low alloy steel in 1M HCl in the absence and presence of *Heliotropium indicum* (HI) inhibitor

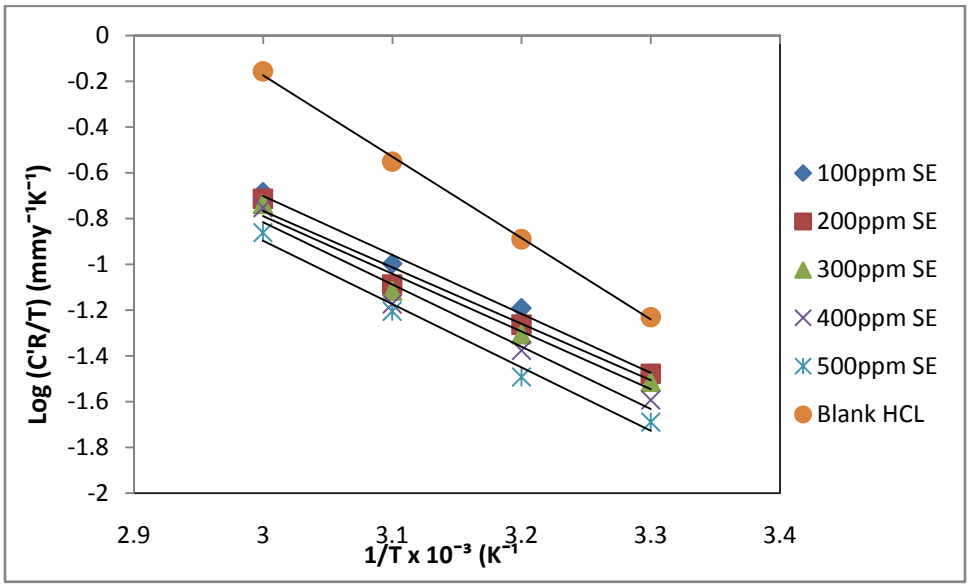


Fig. 4.37: Plot of log (CR/T) versus 1/T for medium carbon low alloy steel in 1M HCl in the absence and presence of *Shell Ensis* (SE) inhibitor

The Kinetic model is another useful tool for explaining the mechanism of corrosion inhibition by any material.Arrhenius plot of log of corrosion rate obtained from gravimetric measurements versus 1/T gives linear graphs with a regression coefficient close to unity and slope equal to $-E_a/2.303R$ ((Figures 4.26 – 4.31). A plot of the logarithm of corrosion rate/T vs 1/T (Transition state) gives straight line with slope equal to $-\Delta H^*/2.303R$ and intercept equal to $In(R/Nh) + \Delta S^*/2.303R$ (Figures 4.32 – 4.37). The calculated values of activation parameters of Chrysophyllum albidium (CA), Heliotropium indicum (HI) and Shell Ensis (SE) inhibitors on the surface of medium carbon low alloy steel in H_2SO_4 and HCl are given in table 4.7.

For varying concentration of inhibitors, as temperature increases the corrosion rate was found to increase. The increase in CR with increase in temperature may be due to the fact that increase in temperature usually accelerates corrosive processes, particularly in media in which gives rise to higher dissolution of metal and volume of hydrogen evolved at higher temperature is significantly higher than at lower temperature.

The apparent E_a values calculated from the plots showed that there is an increase in E_a for uninhibited acids than that of inhibited acid indicating that the formulated inhibitors and standard inhibitor retards the corrosion of medium carbon low alloy steel in the examined medium due to the less competition between forces of absorption and desorption of constituents of the inhibitors. Thus the reactive centers on the inhibitors block the active sites for corrosion resulting in the decrease in corrosion rate and activation energy.

Table 4.7: Values of activation parameters of the formulated and standard inhibitor in 1M H_2SO_4 and HCl

		E_a(KJ/mol)		ΔH^*(KJ/mol)		$-\Delta S^*$(J/mol)	
		H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4	HCl
Blank		75.01	70.73	72.41	68.11	1360	1344
CA	100ppm	57.01	51.19	54.39	48.57	1299	1275
	200ppm	61.74	54.81	59.13	52.19	1312	1285
	300ppm	64.64	64.15	62.03	61.53	1320	1313
	400ppm	66.59	64.02	63.98	61.41	1326	1311
	500ppm	70.15	64.07	67.53	61.41	1336	1309
HI	100ppm	61.40	53.83	58.79	51.21	1313	1283
	200ppm	58.12	49.86	55.51	47.24	1301	1267
	300ppm	64.64	49.35	56.61	46.73	1303	1266
	400ppm	63.83	51.73	61.21	49.11	1317	1273
	500ppm	67.10	50.10	64.48	47.49	1326	1266
SE	100ppm	62.59	51.98	59.98	49.36	1318	1277
	200ppm	64.05	49.87	61.44	47.25	1321	1270
	300ppm	64.95	50.92	62.33	48.30	1323	1273
	400ppm	66.48	54.74	63.87	52.13	1327	1284
	500ppm	67.70	55.61	65.09	52.99	1330	1285

From Table 4.7, the data indicate that the thermodynamic activation energy (E_a) values of the corrosion of medium carbon low alloy steel in 1M H_2SO_4 and HCl in the presence of inhibitors is less than that in the free acid solution and tend to increase as the concentration of inhibitor increased. These values were found to range from 57.01KJ/mol - 70.15 KJ/mol, 61.4 KJ/mol – 67.1 KJ/mol and 62.59 KJ/mol – 67.7 KJ/mol for CA, HI and SE in H_2SO_4 and 51.19 KJ/mol – 64.07 KJ/mol, 53.83 KJ/mol – 50.1 KJ/mol and 51.98 KJ/mol – 55.61 KJ/mol for CA, HI and SE in HCl solution respectively. Thus,$E_a$values of CA, HI and SEin the acidic media support the fact that the constituents of tested inhibitors were absorbed on the low alloy steel surface.

Ebenso *et al.* (2008)reported than values of E_a< 80KJ is indicative of physical absorption while E_a> 80KJ is indicative of chemical absorption. Thus,$E_a$valuesranges are lower than the threshold values of 80KJ required for chemical absorption. This means than absorption is physical absorption. Hence, theclosely high values of$E_a$in the present of CA, HI and SE in $H_2SO_4$and CA in HCL suggest strong physical absorption.This is in good agreement with earlier report by Therese and Vasudha, 2015;Karthik*et al*., 2015; andAejitha*et al*., 2015.

The monotonous increased in $E_a$and ΔH values vary in the same way with inhibitor concentration. Hence, result permits to verify the known thermodynamic relation between $E_a$and ΔH^*. The calculate value of E_a- ΔH in table 4.8 are close to RT is 2.67 KJ/mol which shows the inhibitor acted equally on $E_a$and ΔH. The positive signs of ΔH reflect the endothermic nature of the steel dissolution process suggesting that at high temperature favours the complexation reaction and the same is in good agreement with the increasing stability with temperature. The negative values of -ΔS pointed to a great order produced during the process of activation both in the absence and the presence of the inhibitor imply that the activated complexes in the rate

determining step represent an association rather than a dissociation step, meaning that decrease in disordering takes place on going from reactants to the activated complexes.

4.9.2 Absorption isotherm and thermodynamic Consideration

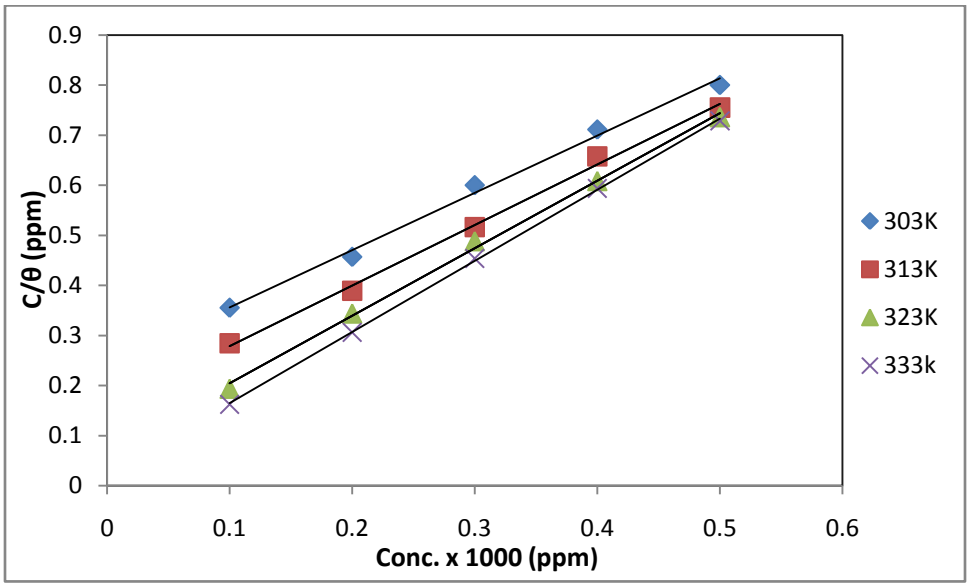


Fig. 4.38: Langmuir absorption isotherm of formulated *Chrysophyllum albidium* (CA) inhibitor in 1M H_2SO_4 solution at different temperatures.

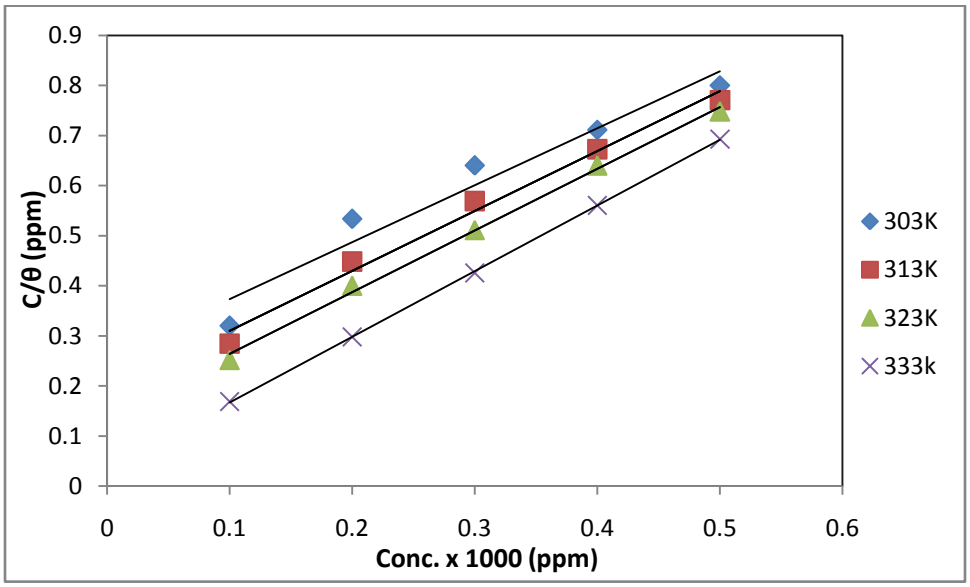


Fig. 4.39: Langmuir absorption isotherm of formulated *Heliotropium indicum* (HI) inhibitor in 1M H_2SO_4 solution at different temperatures.

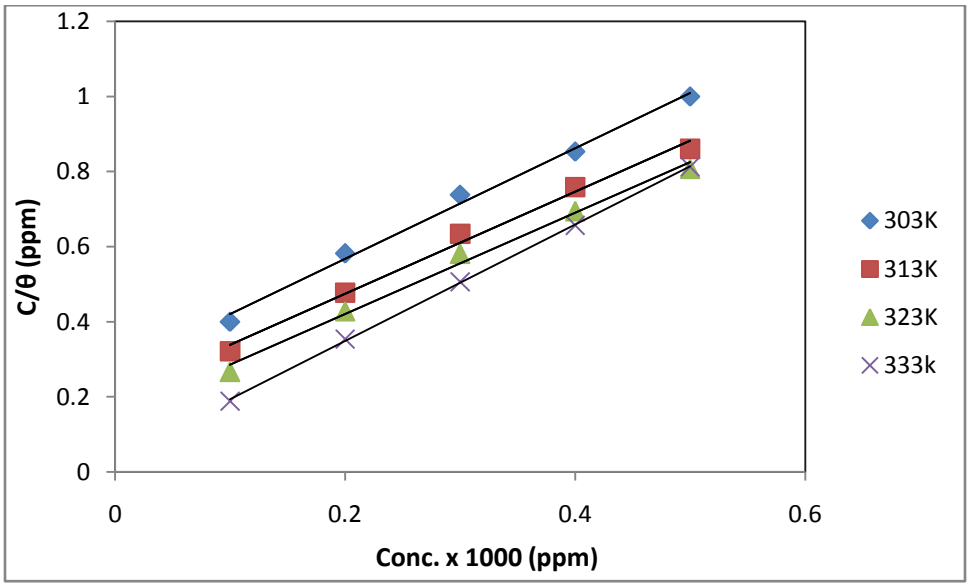


Fig. 4.40: Langmuir absorption isotherm of standard Shell Ensis(SE) inhibitor in 1M H_2SO_4 solution at different temperatures.

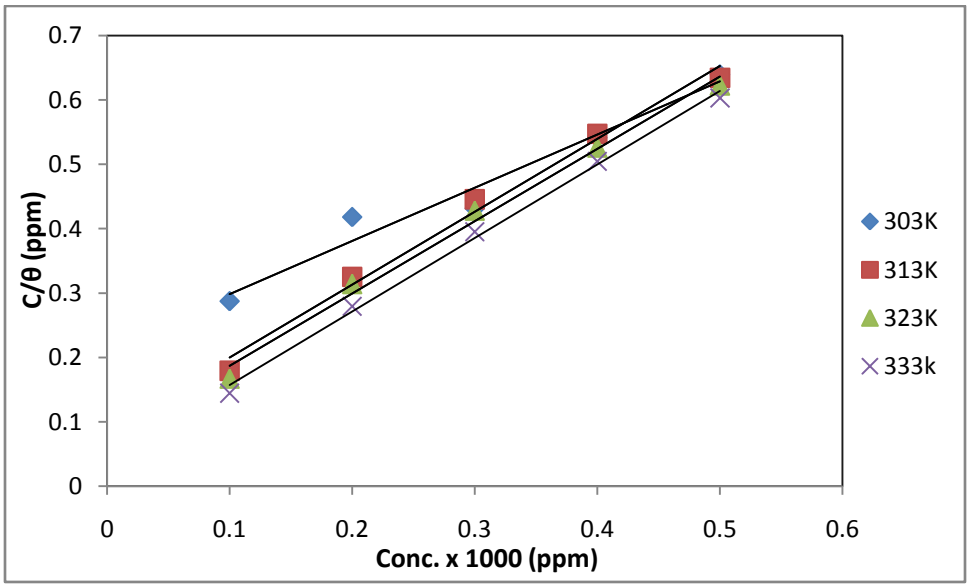


Fig. 4.41: Langmuir absorption isotherm of formulated *Chrysophyllum albidium* (CA) inhibitor in 1M HCl solution at different temperatures.

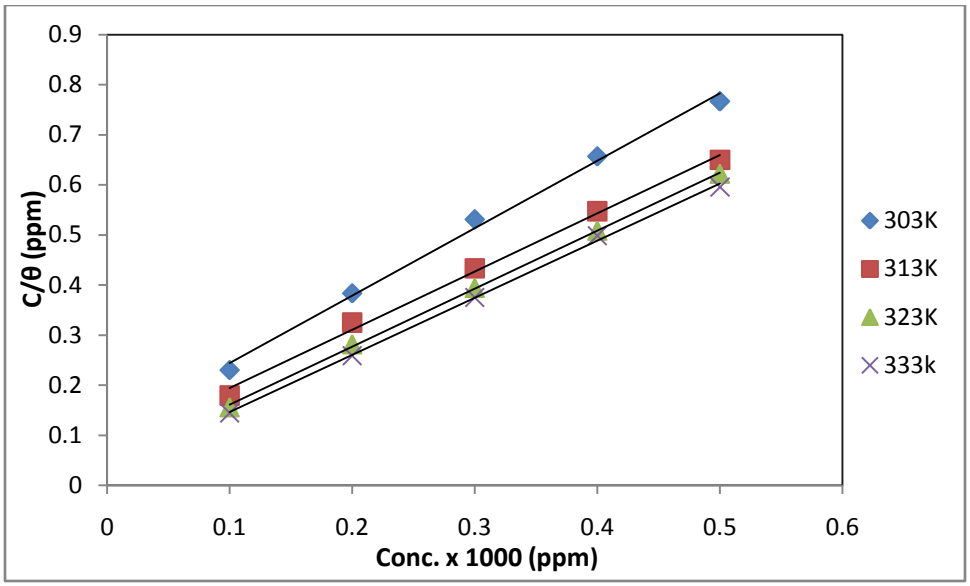


Fig. 4.42: Langmuir absorption isotherm of formulated *Heliotropium indicum* (HI) inhibitor in 1M HCl solution at different temperatures.

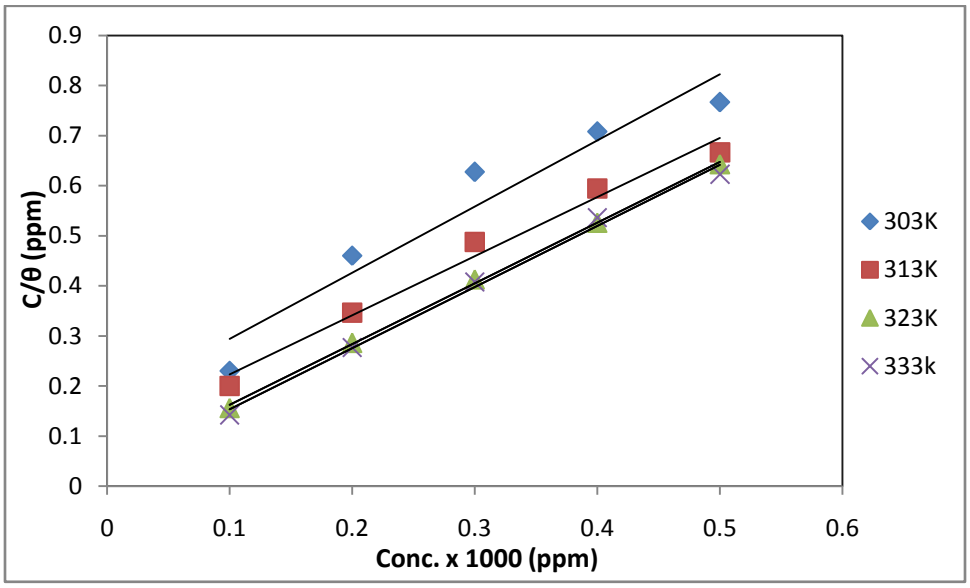


Fig. 4.43: Langmuir absorption isotherm of standard Shell Ensis(SE) inhibitor in 1M HCl solution at different temperatures.

The experimental data obtained with different inhibitor concentrations in the 1M H_2SO_4 and HCl solutions at different temperatures from 303K to 333K were applied to different absorption isotherm equations and themore suitable Langmuir absorption are given in Figures 4.38 – 4.43.

Langmuir absorption isotherm model best described than the most frequently used such as Temkin and Freundlish isotherms. The correlation coefficient (R2) was used to choose the adsorption isotherm that best fits the experimental data and it is found that the adsorption process generally follows the Langmuir adsorption isotherm (R2 > 0.99). The other isotherms viz. Temkin and Freundlish isotherms do not fit the data significantly. The calculated thermodynamic adsorption parameters are listed in Tables 4.8 – 4.9.

Table 4.8: Values of thermodynamic adsorption parameters of the formulated and standard inhibitors in 1M H_2SO_4

Temp (K)		K_{ads}	ΔG^0_{ads}	**Correlation**		
				Langmuir (R^2)	Temkin (R^2)	Freundlish (R^2)
CA	303	4.13	-13.69	0.994	0.995	0.983
	313	6.33	-15.26	0.997	0.984	0.981
	323	14.41	-17.95	0.998	0.991	0.996
	333	43.10	-21.54	0.999	0.981	0.979
HI	303	3.85	-13.52	0.996	0.934	0.968
	313	5.26	-14.77	0.988	0.983	0.918
	323	7.11	-16.05	0.997	0.996	0.995
	333	27.78	-20.32	1	0.949	0.939
SE	303	3.66	-13.39	0.994	0.993	0.998
	313	4.93	-14.60	0.992	0.992	0.996
	323	6.61	-15.86	0.992	0.998	0.997
	333	25.84	-20.12	1	0.994	0.994

Table 4.9: Values of thermodynamic adsorption parameters of the formulated and standard inhibitor in 1M HCl

Temp (K)		K_{ads}	ΔG^0_{ads}	**Correlation**		
				Langmuir (R^2)	Temkin (R^2)	Freundlish (R^2)
CA	303	4.64	-13.98	0.996	0.960	0.966
	313	11.53	-16.82	0.990	0.947	0.967
	323	13.39	-17.75	0.992	0.930	0.946
	333	23.42	-19.85	0.996	0.918	0.930
HI	303	9.14	-15.69	0.995	0.992	0.997
	313	12.84	-17.09	0.996	0.975	0.984
	323	22.32	-19.13	1	0.996	0.994
	333	31.25	-20.65	0.999	0.957	0.953
SE	303	6.17	-14.70	0.992	0.724	0.749
	313	9.55	-16.32	0.985	0.936	0.963
	323	24.57	-19.38	0.999	0.995	0.997
	333	32.15	-20.71	0.995	0.758	0.775

The negative values of ΔG^0_{ads} suggest that the adsorption of the inhibitors on steel surface is spontaneous. Generally, ΔG^0_{ads} values between 0 and -20kJ/mol are associated with electrostatic interactions between the charged molecules and charged metal surface (physisorption). The values of ΔG^0_{ads} around - 40kJ mol-1 or more negative involve charge sharing or transfer of charge from the inhibitor molecules to the metal surface to form a coordinate-covalent bond, (chemisorptions).

In this work, ΔG^0_{ads} negative values of the free energies of adsorption suggested that the adsorption of the inhibitors onto the steel was a spontaneous process. Its increase with temperature revealed that the adsorption of inhibitors on the surface of the steels was more favourable with increase in experimental temperatures as established by Noor *(*2009). Although, ΔG^0_{ads} values are within the range and slightly higher than -20kJ/mol, which indicates that the inhibitor constituents adsorbed on steel surface involve physical and chemical process. Hence, the higher values of K_{ads}at a temperature close to 333k are a clear indication that inhibitor constituents are strongly absorbed on the metal surface, this is in good agreement with value of surface coverage obtained.

4.9.3 Linear PolarizationResistance Test

The values of medium carbon steels electrochemical parameters such as corrosion potential (E_{corr}), current density (I_{corr}), tafel slopes (β_c and β_a), resistance polarization (R_p) and inhibition efficiency (η%) obtained for electrochemical measurements in 1M $H_2SO_4$and HCL are tabulated in Table 4.10 – 4. 11.

From the record Ecorr values obtained from the tests, which show a mixed mode of inhibition as they do not increase or decrease in a regular manner from the blank value. The mixed mode of inhibition is again proved by the values of βcand β_a, which also do not increase or decrease in a regular manner (Kumar *et al.*, 2010**)**. The steady decrease in I_{corr} values with increase in inhibitor concentration is an indication of decrease in corrosion reaction because corrosion current is proportional to the magnitude of corrosion reaction ininhibitor concentration and shown by the increased of Rp values.

Table 4.10: Potentiodynamic polarization and LPR parameters for corrosion of steel sample in 1.0M H_2SO_4 solution containing different concentrations of formulated inhibitors and standard inhibitor.

Inhibitor	Conc.(ppm)	$-E_{corr}$ (mV)	I_{corr} (mA cm^2)	$-\beta_c$ (mV dec^{-1})	β_a (mV dec^{-1})	R_p (ohm cm^2)	η%
Blank	0	910	2.611	123	96	8.967	0
	100	978	1.678	168	623	15.663	35.7
C.A	200	962	0.573	89	114	9.972	78.1
	300	959	0.336	73	681	22.426	87.1
	400	940	0.116	65	47	26.913	95.6
	500	944	0.106	38	106	30.043	95.9
	100	1046	0.307	82	268	23.348	88.2
H.I	200	968	0.268	50	114	14.852	89.7
	300	1005	0.157	48	95	23.255	94.0
	400	997	0.150	42	132	24.175	94.3
	500	986	0.129	49	108	30.005	95.1
	100	1028	0.786	175	156	11.967	69.9
S.E	200	1081	0.622	154	123	12.574	76.2
	300	1147	0.577	313	201	24.207	77.9
	400	1071	0.367	106	114	17.078	85.9
	500	1043	0.291	76	96	16.613	88.9

Table 4.11: Potentiodynamic polarization and LPR parameters for corrosion of steel sample in 1.0M HCl solution containing different concentrations of formulated inhibitors and standard inhibitor.

Inhibitor	Conc. (ppm)	$-E_{corr}$ (mV)	I_{corr} (mA cm^2)	$-\beta_c$ (mV dec^{-1})	β_a (mV dec^{-1})	R_p (ohm cm^2)	η%
Blank	0	949	0.610	232	211	20.801	0
	100	884	0.530	169	406	25.489	13.1
C.A	200	919	0.021	74	177	28.860	96.6
	300	846	0.017	94	166	40.633	97.2
	400	893	0.012	83	149	53.705	98.0
	500	901	0.011	38	105	53.596	98.2
	100	834	0.029	118	205	28.929	95.1
H.I	200	940	0.024	74	138	22.230	95.9
	300	912	0.024	89	112	22.841	95.9
	400	906	0.034	120	129	20.903	94.4
	500	950	0.025	104	296	35.832	96.0
	100	957	0.313	66	72	12.725	48.6
S.E	200	985	0.099	180	218	12.528	83.8
	300	865	0.078	126	117	8.8984	87.2
	400	970	0.053	92	106	10.763	91.3
	500	958	0.023	134	213	40.566	96.2

All the electrochemical parameters in the tables (4.11 – 4.12) confirm that the corrosion control depends on the concentration of the inhibitor, which is evident from their polarization curves (figures 4.44 –4.49).

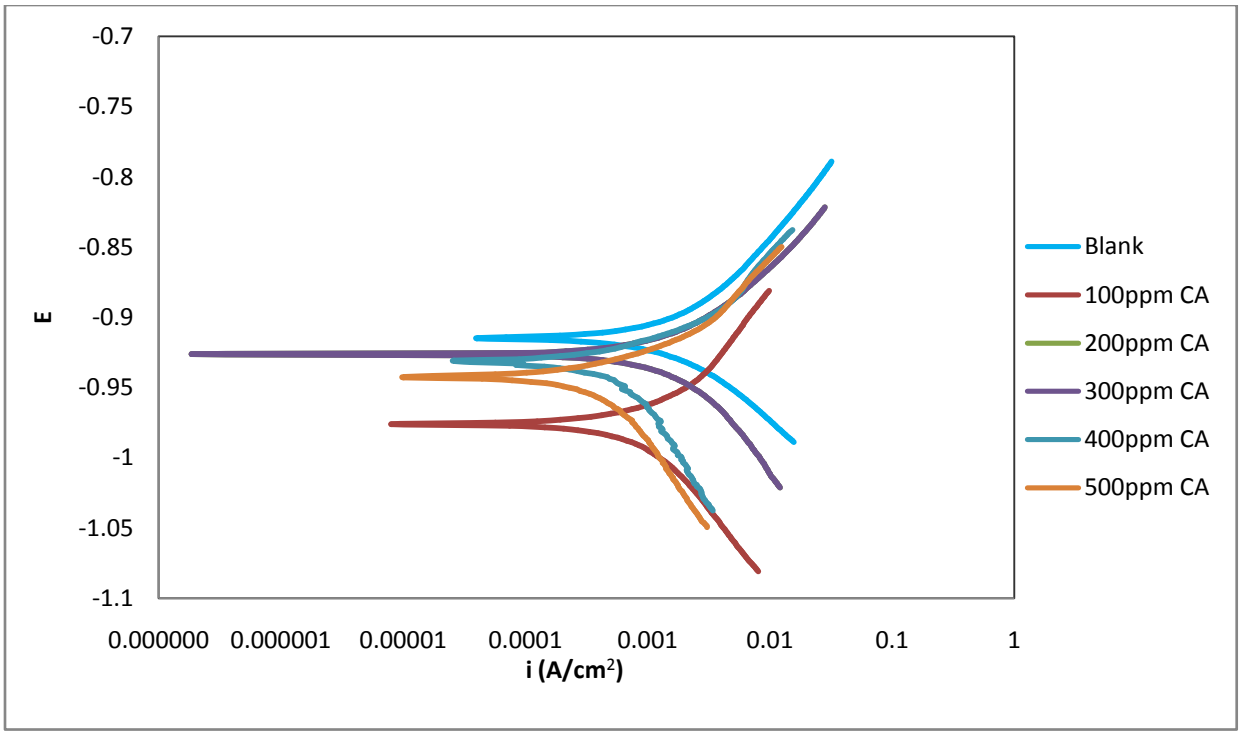


Fig. 4.44: Polarization curve of the corrosion of steel sample in 1.0M H_2SO_4 solution in the presence of formulated inhibitor of Chrysophyllum Albidium (CA).

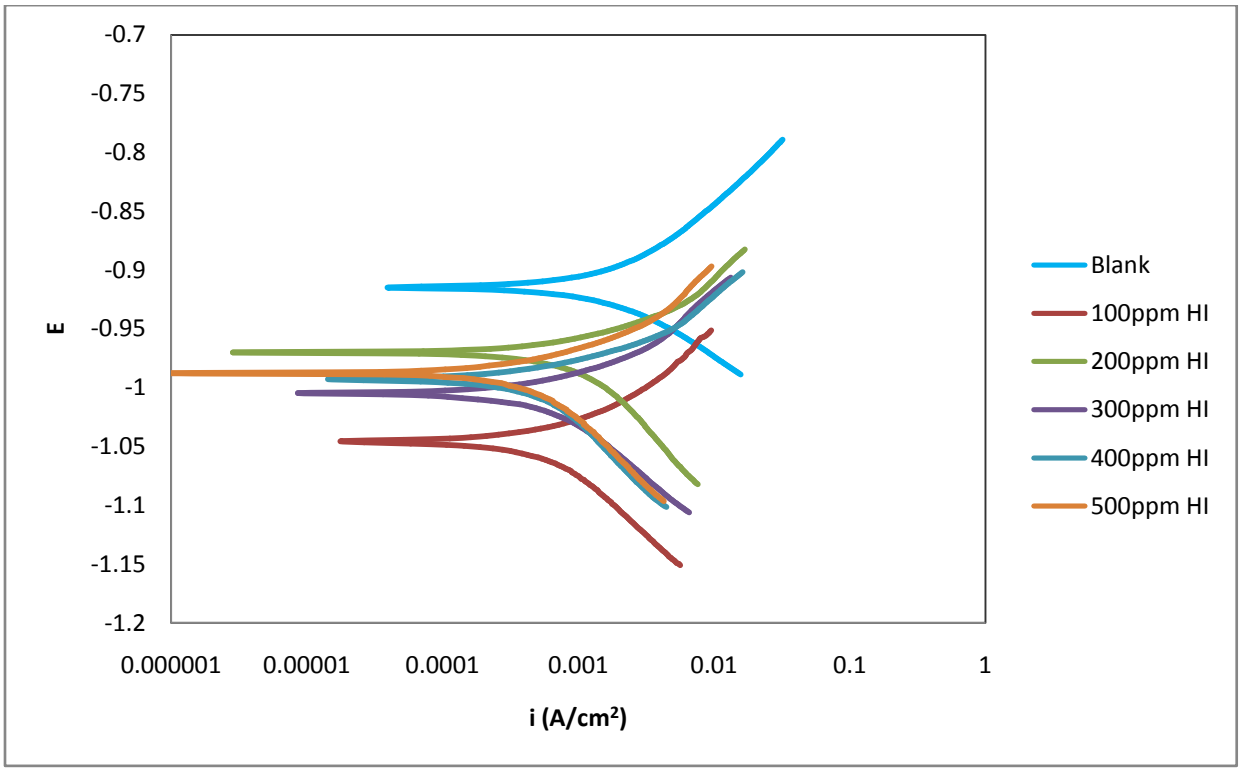


Fig. 4.45: Polarization curve of the corrosion of steel sample in 1.0M H_2SO_4 solution in the presence of formulated inhibitor of Heliotropium Indicum (HI)

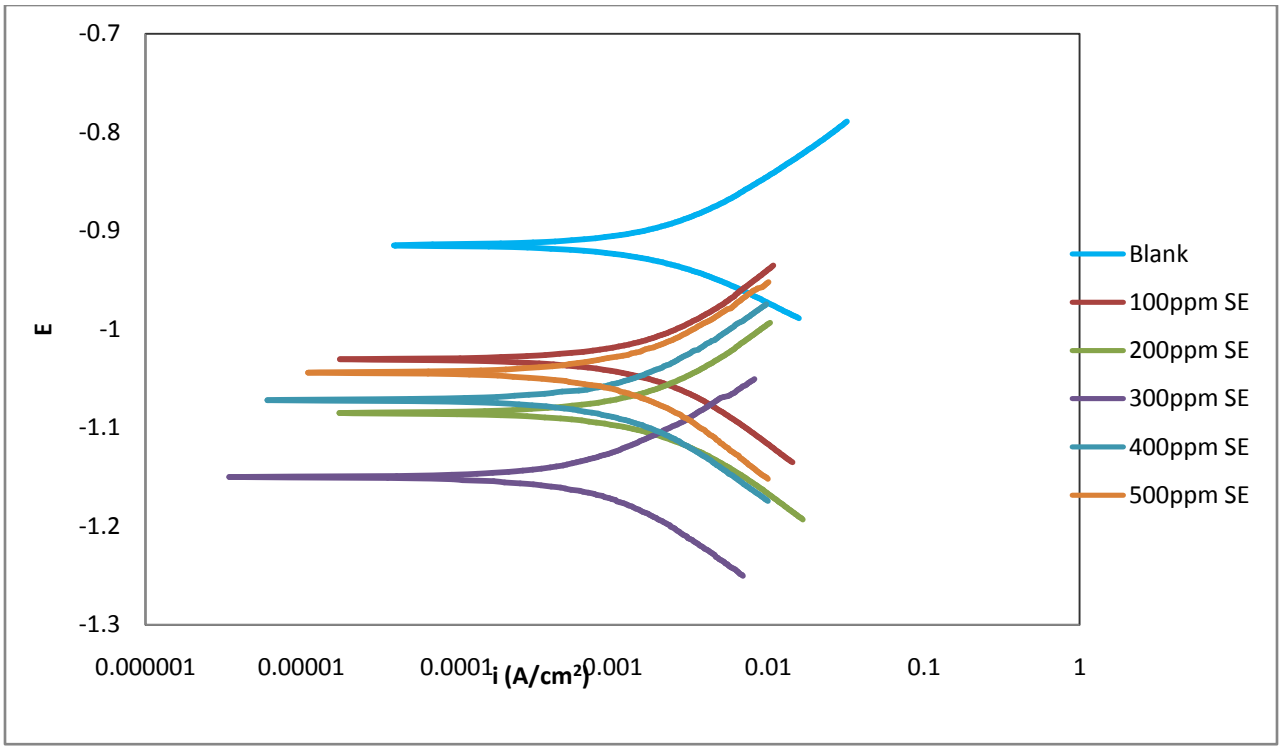


Fig. 4.46: Polarization curve of the corrosion of steel sample in 1.0M H_2SO_4 solution in different concentration of the standard inhibitor (Shell Ensis;SE).

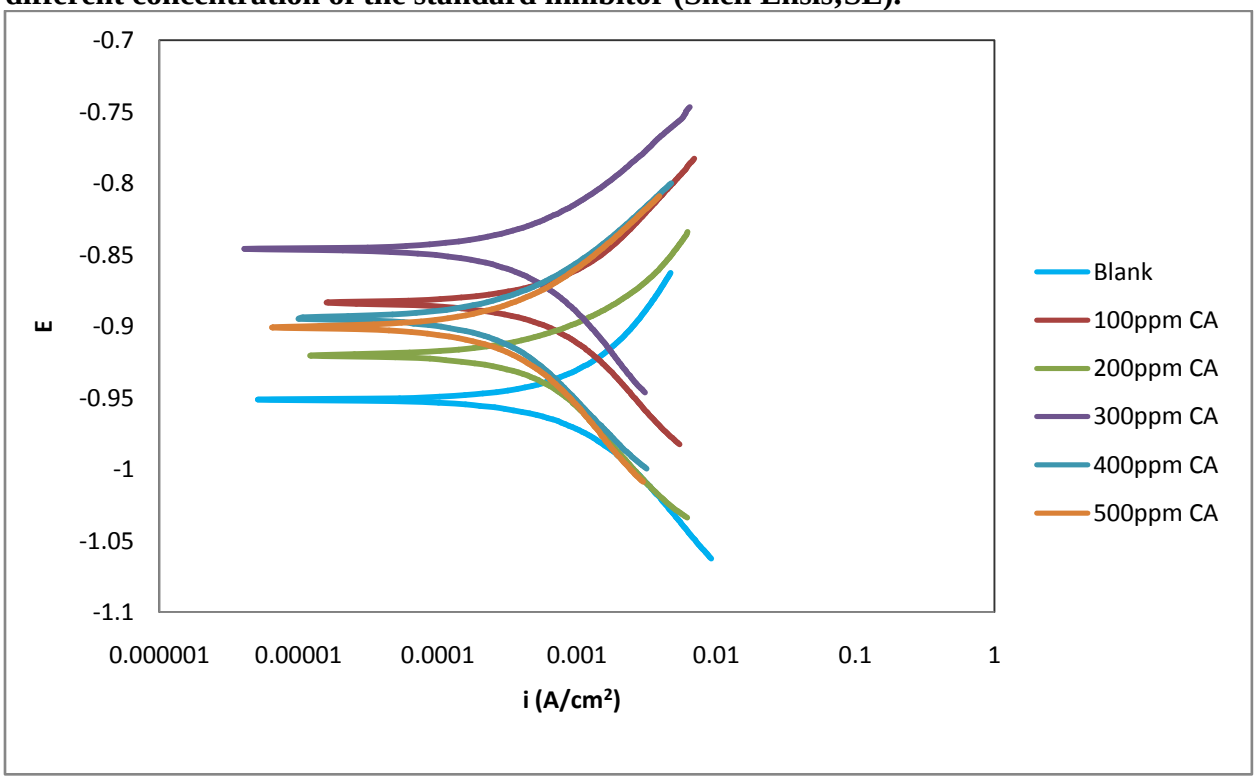


Fig. 4.47: Polarization curve of the corrosion of steel sample in 1.0M HCl solution in the presence of formulated inhibitor of Chrysophyllum Albidium (CA).

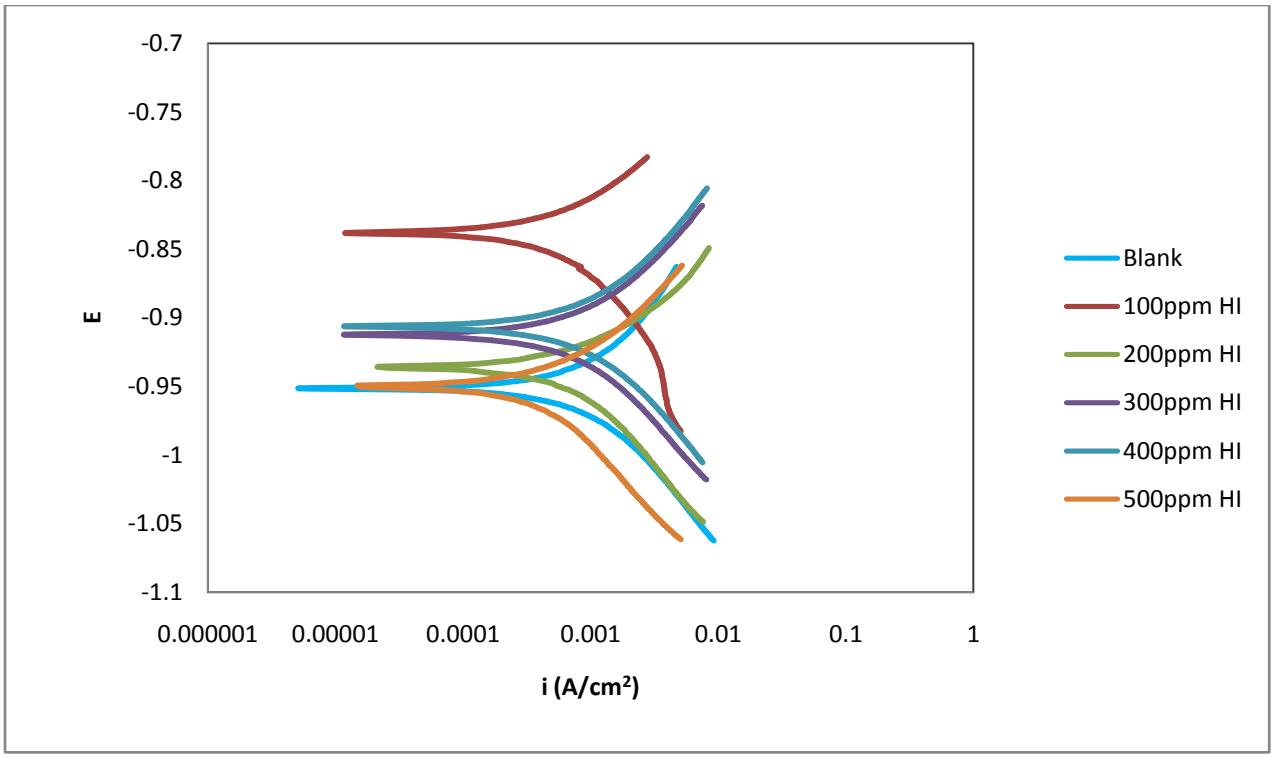


Fig. 4.48: Polarization curve of the corrosion of steel sample in 1.0M HCl solution in the presence of formulated inhibitor of Heliotropium Indicum (HI) Inhibitor.

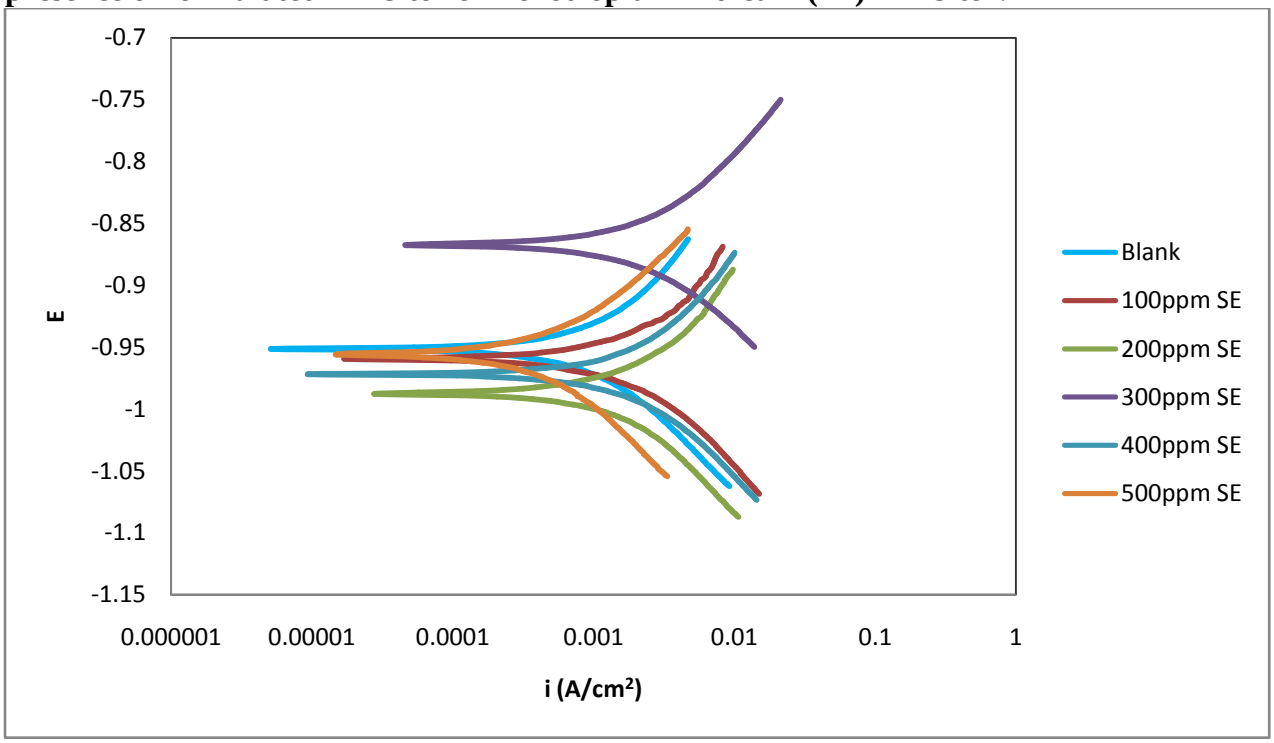


Fig. 4.49: Polarization curve of the corrosion of steel sample in 1.0M HCl solution in different concentration of the standard inhibitor (Shell Ensis ; SE).

When medium carbon steel (blank) is immersed in 1M H_2SO_4, the corrosion potential and corrosion current are 910mV and 2.611 x 10^{-3}A cm^2 against SCE (Saturated calomel electrode). Thus, asChrysophyllum Albidium concentration increases the corrosion potential shifts towards more positive values of 978 mV indicating that CA plays a stronger role in suppressing the anodic reaction in 1M H_2SO_4 (Obot and Madhankumar, 2014). It is instructive to note that similar results were obtained with Heliotropium indicum and Shell Ensis SX inhibitors (Figs. 4.45– 4.46); that is the Ecorr shifts towards more positive values and both anodic and cathodic regions were affected in 1M H_2SO_4.This suggests that this formulation controls the anodic reaction predominantly.

The inhibitive nature in the absence and presence ofinhibitors in 1M H_2SO_4 system is associated with increase inresistance polarization ((R_p)) values from 8.967 ohm cm^2 in the absence of inhibitor (blank) to 30.04, 30.01 and 16.6 ohm cm^2 in the presence of Chrysophyllum albidium, Heliotropium Indicum and Shell Ensis at 500ppm respectively, this suggests that a protective film was formed on the metal surface as the corrosion current decreases from 2.611 (blank) to 0.106 in the presence of Chrysophyllum albidium at 500ppm (Rajendrans, 2002; Selvarani, 2004; Sribharathy, 2011).

However,similar trends were observed for Heliotropium indicum and Shell Ensis with corrosion current decreasing to 0.129 and 0.291 x 10^{-3}A cm^2 respectively at optimum concentration. C. Albidium and H. Indicum did not onlycomparefavourable but also performed better in the HCl as compared to H_2SO_4 solution with increase in inhibition efficiency from 95.9 to 98.2 and 95.1 to 95.9.

4.10 **SEM Analysis**

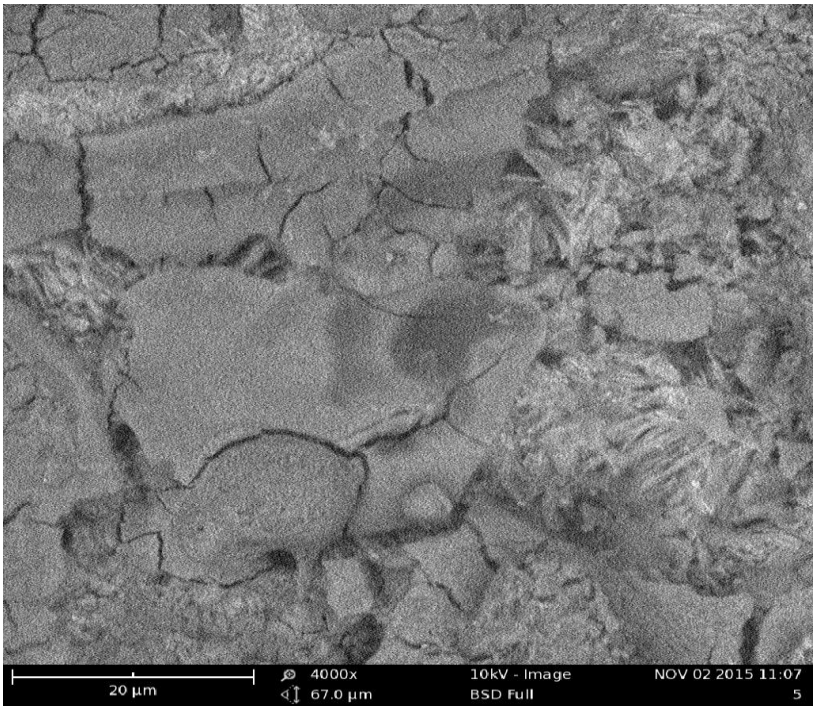


Plate 4.2: SEM image of steel in 1M HCl solution in the absence of inhibitor

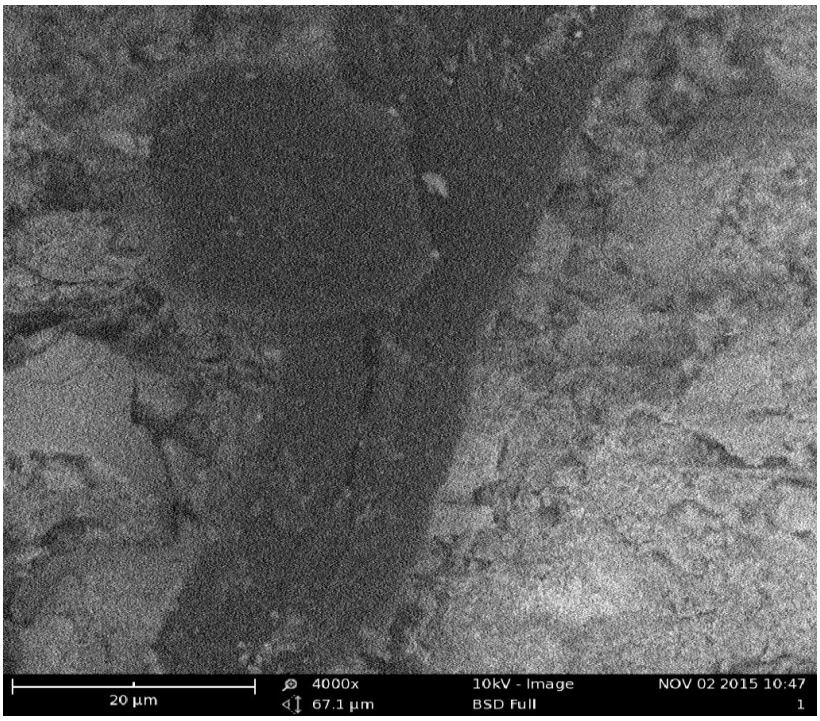


Fig. 4.3: SEM image of steel in 1M HCl solution in presence of formulated inhibitor of Chrysophyllum albidium (CA).

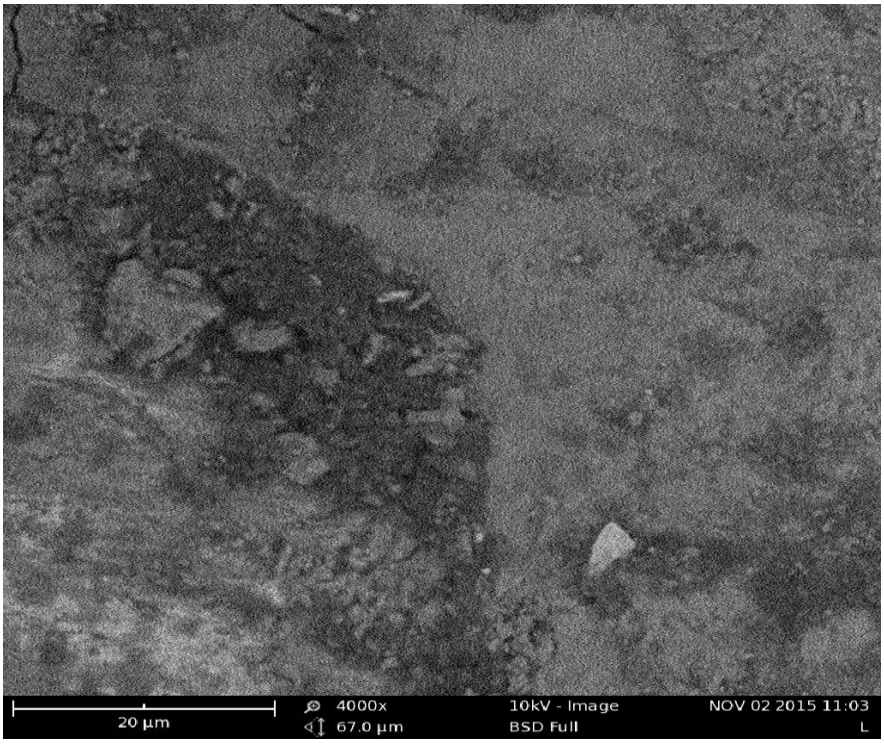


Fig. 4.4: SEM image of steel in 1M HCl solution in presence of formulated inhibitor of Heliotropium indicum (HI).

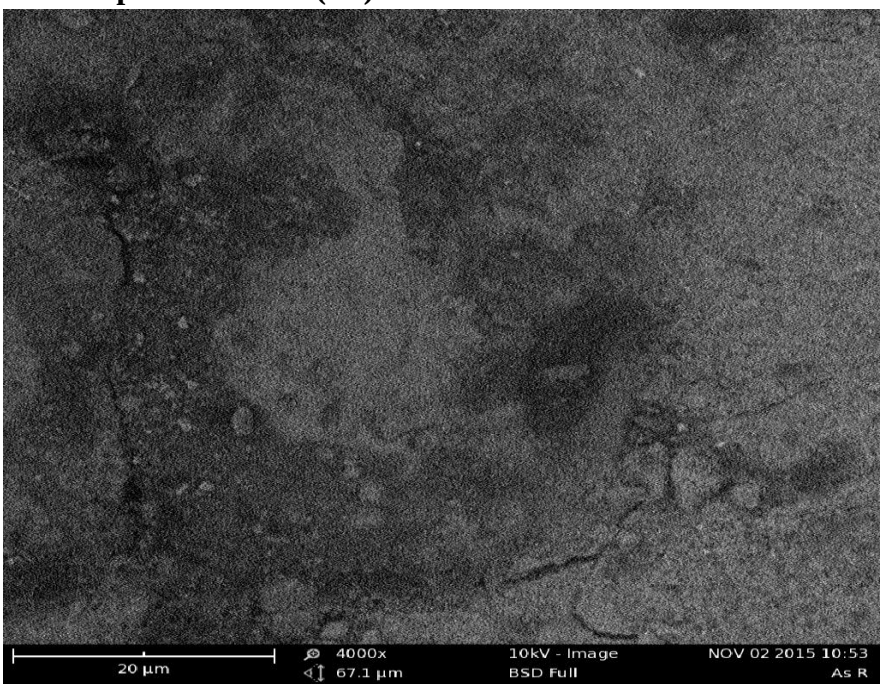


Fig. 4.5: SEM image of steel in 1M HCl solution in presence of Shell Ensis standard inhibitor.

Plates 4.2 - 4.5 showed the Scanning Electron Microscope images of the medium carbon low alloy steel before and after corrosion tests. Plate 4.2 shows the roughness of the metal surface which indicates the corrosion of medium carbon low alloy steel in HCl acid solution was severely attacked. Plates 4.3 – 4.5 shows the appearance of smooth medium carbon low alloy steel surfaces after the addition of tested inhibitors to the acid solution. This examination indicates that corrosion rate is reduced in the presence of inhibitors. The active films formed protects the surface of the medium carbon low alloy steel become less susceptible to attack, which is good agreement with work of Suileman*et al.* (2012) and Lebrieni*et al.* (2011).

However, appreciable corrosion inhibition was observed when compared with the absence of inhibitors and the as-received medium carbon low alloy sample (Appendix V). However, the greatest magnitude of adsorption of inhibitor molecules was in in order of HCl: Plate 4.3 (CA) >Plate 4.4 (HI) > Plate 4.5 (SE), which showed the highest features of surface coverage obtained with the addition of formulated inhibitor of Chrysophyllum albidium (CA) in this study. These observations are very much in agreement with results obtained for the weight loss method.

4.11 Results of Mechanical Properties Tests

Tables 4.12 - 4.14 gave values of the mechanical properties (i.e. impact, tensile and hardness) of test specimensin the presence and absence of inhibitor after 21 days of immersion in acidic media. The hardness value of the inhibited is greater than that of uninhibited samples. This shows that the effect of corrosion on the hardness of the test specimen is higher on the unhibited than the inhibited sample which means that softer corrosion products are on the surface of the unhibited samples (Table 4.12).

Tables 4.12: Hardness values of medium carbon low alloy steel after 21 days of immersionperiod

Test Condition	Average Hardness Values (HB)	
	Corrosive medium H_2SO_4	Corrosive medium HCl
In the absence of inhibitor	142.84	197.3
In the presence of Chrysophyllum Albidium (CA)	223.73	234.69
In the presence of Heliotropium Indicum (HI)	219.96	236.70
In the presence of Shell Ensis SX (SE)	211.51	233.45

The decrease in impact and tensile strength is attributed to the reduction in area of the steel sample as a result of gradual weight loss (Tables 4.13 -4.14). It is revealed that the mechanical properties of the steel reduced drastically in uninhibited media but improve with inhibitive ones. This implies that the formulated inhibitors namely Chrysophyllum albidium and Heliotropium indicum and Shell Ensis standard inhibitor effectivelylowers the corrosion rate of medium carbon steel in the two media.

Also, Tables 4.12 - 4.14 showed that H_2SO_4strongly attack the steel specimens which in turn reduce the strength and hardness of the materials compare to HCl solution. This is in agreement with previous works by Faci (2015) and Fatai (2015).

Tables 4.13: Impact strength of low alloy steel after 21 days of immersion period

Test Condition	Impact Strength (Joules)	
	Corrosive Medium H_2SO_4	Corrosive medium HCl
In the absence of inhibitor	48.70	52.60
In the presence of Chrysophyllum Albidium (CA)	55.76	63.72
In the presence of Heliotropium Indicum (HI)	56.70	61.52
In the presence of Shell Ensis SX (SE)	54.50	61.52

Tables 4.14: Tensile strength of low alloy steel after 21 days of immersion

Test Solution	Tensile Values (Nmm^{-2})	
	Corrosive medium H_2SO_4	Corrosive medium HCl
In the absence of inhibitor	342.72	484.66
In the presence of Chrysophyllum Albidium (CA)	440.12	614.84
In the presence of Heliotropium Indicum (HI)	436.61	598.41
In the presence of Shell Ensis SX (SE)	428.78	569.40

CHAPTER FIVE

5.0 CONCLUSION AND RECCOMENDATION

5.1 Conclusion

This work encompassesbiochemical extraction and characterization of two plant extracts, formulation of the produced extracts into inhibitors and testing the formulated inhibitors for the protection of low alloy steel in H_2SO_4 and HCl media. Based on the results obtained the following conclusions could be drawn:

(i) Phytochemical screeningof the plant leavesshow presence ofphytochemical constituents such as saponins, tannins, alkaloids and flavonoids, in these orderupto percent values for Chrysophyllum albidium (CA) as 16.65%, 1.65%, 0.62% and 86.44% while Heliotropium indicum (HI) has 24.90%, 2.05%, 1.04% and 96.25% respectively, which are a good indicator that they can be used as corrosion inhibitor.

(ii) Physico-chemical properties of the two plant extracts showed that they are slight acidic, non-toxic, biodegradable hence environmental friendly. The formulated plant extracts attained upto 95 percent biodegradation while standard Shell Ensis SX (SE) gives 62 percent extent of biodegradation as established in the OECD marine BOD tests.

(iii)The gravimetric basedmass loss experiments showed decreased corrosion rates with increase in inhibitors concentration and exposure time. Potentiodynamic studies showed higher value of inhibition efficiencies percent of 98.2% (CA), 96.0% (HI) and 96.2% (SE)obtained informulated inhibitors at ambient temperature; however this could not be reproduced during gravimetric based mass loss experimentdue its environment dependent nature of this method.

(iv) The inhibition efficiencies were observed to increase with increase in concentration of inhibitors for both gravimetric basedmass loss experiments and electrochemical measurements.

(v) Potentiodynamic polarization curves reveal that the two plant extracts affected both anodic and cathodic processes, i.e., these are mixed-type inhibitors.

(vi) The adsorption of the inhibitors onto the steel surfaces is an endothermic process, and in the process both physical and chemical adsorption takes place and are best described by Langmuir absorption isotherms obtained from the kinectic study.

5.2 Recommendations

(i) Potentiodynamic polarization studies of the action of the inhibitors invaryingH_2SO_4 and HCl acid concentrations at elevated temperature is recommended so as to verify the kinetic and thermodynamic models arrived at in this work.

(ii) The extracts of Chrysophyllum albidium and Heliotropium indicum will serve as effective and eco-friendly inhibitors, therefore could be used as corrosion inhibitors in the processes of oil well acidizing, chemical cleaning, acid pickling and descaling of medium carbon steels.

(iii) Acute toxicity (LC_{50}) and OECD 501tests so as to further verify the biodegradability limits established at in this work.

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APPENDICES

Appendix I: - Dilutions of Stock Solution

(a)Preparations of 1M HCl Solution

Density of Concentrated HCl = 1.18g/ml

Molecular weight of HCl = 36.461g/mole

Strength of Analytical Grade of HCl = 32%

$$\text{Molarity (Mol/dm}^3\text{)} = \frac{Mole(mol)}{Volume(dm^3)} \quad \text{..... (eq. 11)}$$

$$\text{Molarity (Mol/dm}^3\text{)} = \frac{32*1000*1.16}{100*36.5} = 10.2\ \text{M}$$

Therefore for 1M HCl stock solution of 1000ml solution

Using the relation: $C_AV_A = C_BV_B$ .....(eq. 11b)

Where:

C_A = Concentration of concentrated(original) solution

V_A = Volume of concentrated(original) solution

C_B = Concentration of desired (final) solution

V_B = Volume of desired (final) solution

$C_AV_A = C_BV_B$

$10.2\ \text{M} * V_A = 1\text{M} * 1000\text{ml}$

$V_A = 98.04\text{ml}$

98.0ml volume of HCl required to make1000ml of 1M HCl solution

(b) Preparation of 1M H_2SO_4 Solution

Density of Concentrated H_2SO_4 = 1.83g/ml

Molecular weight of H_2SO_4 = 98.073g/mole

Concentrated of Analytical Grade of H_2SO_4 =95%

Usingequation 11a therefore:

$$\text{Molarity (Mol/dm}^3\text{)} = \frac{95*1000*1.83}{100*98.073} = 17.8\ \text{M}$$

Therefore for 1M H_2SO_4 of 1000ml solution

Usingequation 11b therefore:

$$17.82 * V_A = 1\text{M} * 1000\text{ml}$$

$$V_A = 56.12\text{ml}$$

56.0 ml volume of H_2SO_4 required to make 1000ml of 1M H_2SO_4 solution

Appendix II: - Determination of Inhibitors Formulation

Concentration: refers to the amount of solute that dissolved in a solvent and sometimes given in percent (weight of inhibitor relative to the volume of test solution).

Solute: refers to crude extracts (solid) that is added to a stock solution (solvent)

Solvent: refers to the substance which does the dissolving (typically a liquid)

$$\text{Concentration} = \frac{\text{mass of solute (g)}}{\text{volume of the solution (L)}} \text{ (g/L)} \quad \text{(eq. 12)}$$

Note: gram (solute) per litre (solvent) is also refer to as part per thousand (ppt)

Using weight per volume of solution comparisons and converting to part per millions (ppm)

$$\text{Concentration (ppm)} = \frac{\text{mass of solute (g)}}{\text{volume of the solution (L)}} * 1000$$

Therefore:

0.1g/L:

$$\text{Concentration} = \frac{0.1\text{g}}{1\text{L}} * 1000$$

$$= 100\text{ppm}$$

0.2g/L:

$$\text{Concentration} = \frac{0.2\text{g}}{1\text{L}} * 1000$$

$$= 200\text{ppm}$$

0.3g/L:

Concentration= $\frac{0.3g}{1L}$ *1000

= 300ppm

0.4g/L:

Concentration= $\frac{0.4g}{1L}$ *1000

= 400ppm

0.5g/L:

Concentration= $\frac{0.5g}{1L}$ *1000

= 500ppm

Appendix III: - Corrosion Rate (C.R) and Inhibitor Efficiencies (I.E)

$$\textbf{\textit{Corrosion Rate}}\ (CR) = \frac{87.6 * \Delta W}{\rho * A * t}(mmpy) \qquad \text{…….. (Eq. 6)}$$

Parameters for the medium carbon low alloy steel sample are:

$\rho = 7.98 g/cm^3$

$A = 14.18 cm^2$

Average mass: 34 grams

Volume = $4.26\ cm^3$

ΔW = weight loss (Initial weight – Final weight)

Therefore

Blank HCl at 72 hours of immersion time

Where $\Delta W = 0.885g \approx 885mg$

$$Corrosion\ Rate\ (CR) = \frac{87.6 * 885}{7.98 * 14.18 * 72}(mmpy)$$

Corrosion Rate (CR) = $9.515591\ mmy^{-1}$

Blank 100ppm CA in HCl at 72 hours of immersion time

Where $\Delta W = 0.042g \approx 42\ mg$

$$Corrosion\ Rate\ (CR) = \frac{87.6 * 42}{7.98 * 14.18 * 72}(mmpy)$$

Corrosion Rate (CR) = $4.515874\ mmy^{-1}$

Inhibitor Efficiencies $IE\ (\%) = \frac{9.51559 - 4.515874}{9.515591} * 100 = 34.78\ \%$ …… (Eq. 7a)

The above calculation was repeated for all concentration of inhibitors formulation to obtain CR and IE respectively as shown in Tables 1 - 14

Table 1: Corrosion behaviour of medium carbon steel samples in 1M HCl solution in the absence of any inhibitor at varying immersion time

Exposure Time(Hrs)	**Initial Weight** (W_1)	**Final Weight**(W_2)	**ΔW** (gm)	**C.R** (mmpy)
72	32.01	31.125	0.885	9.515591
144	30.89	29.811	1.079	5.800747
216	31.298	29.972	1.326	4.752419
288	31.969	30.286	1.683	4.523938
360	30.89	28.831	2.059	4.427707
432	30.11	27.795	2.315	4.148511
504	31.476	29.023	2.453	3.767836

Table 2: Corrosion behaviour of medium carbon steel samples in 1.0M H_2SO_4 solution in the absence of any inhibitor at varying immersion time

Exposure Time(Hrs)	**Initial Weight** (W_1)	**Final Weight**(W_2)	**ΔW** (gm)	**C.R** (mmpy)
72	32.01	26.143	5.867	63.08245
144	30.89	22.992	7.898	42.45996
216	31.298	22.803	8.495	30.44631
288	31.969	23.284	8.685	23.34545
360	30.89	22.099	8.791	18.90431
432	30.11	21.152	8.958	16.05286
504	31.476	22.383	9.093	13.96695

Table 3: Corrosion behaviour of steel sample in in 1.0M H_2SO_4 solution in the presence of formulated inhibitor of *Chrysophyllum albidium* (CA) at varying immersion time

Conc. (ppm)	**Time** (Hrs)	**Initial** W. (W_1)	**Final W.** (W_2)	ΔW (g)	C.R (mmpy)	Θ	I. E. (%)
100ppm CA	72	31.558	28.581	2.977	32.008942	0.492586	49.25856
	144	30.327	25.951	4.376	23.525551	0.445936	44.59357
	216	30.579	25.31	5.269	18.884237	0.379753	37.97528
	288	31.143	25.299	5.844	15.708789	0.327116	32.71157
	360	31.66	25.611	6.049	13.007866	0.31191	31.19099
	432	30.399	24.21	6.189	11.090771	0.309109	30.91092
	504	31.53	25.294	6.236	9.5785673	0.314198	31.41977
200ppm CA	72	31.23	28.641	2.589	27.837135	0.558718	55.87183
	144	31.126	27.051	4.075	21.907363	0.484047	48.40466
	216	31.175	26.108	5.067	18.160263	0.403531	40.35315
	288	31.175	25.75	5.425	14.582509	0.37536	37.53598
	360	30.61	24.998	5.612	12.068135	0.36162	36.16198
	432	30.772	24.949	5.823	10.434894	0.349967	34.99665
	504	31.305	25.214	6.091	9.3558456	0.330144	33.01441
300ppm CA	72	31.85	29.706	2.144	23.05246	0.634566	63.45662
	144	31.071	27.323	3.748	20.149398	0.525449	52.54495
	216	30.083	25.399	4.684	16.787581	0.448617	44.86168
	288	31.61	26.602	5.008	13.461604	0.423374	42.33736
	360	32.391	27.155	5.236	11.259578	0.404391	40.43909
	432	31.793	26.452	5.341	9.5711432	0.403773	40.37732
	504	31.428	25.716	5.712	8.7736973	0.371824	37.18245
400ppm CA	72	30.268	28.279	1.989	21.385887	0.660985	66.09852
	144	32.535	29.057	3.478	18.697867	0.559635	55.96354
	216	31.397	27.086	4.311	15.450739	0.492525	49.2525
	288	30.142	25.39	4.752	12.773471	0.45285	45.28497
	360	33.19	28.303	4.887	10.509083	0.444091	44.40905
	432	30.679	25.663	5.016	8.9887389	0.440054	44.00536
	504	31.801	26.475	5.326	8.1807969	0.414275	41.42747
500ppm CA	72	30.531	28.733	1.798	19.33224	0.69354	69.35401
	144	31.651	28.403	3.248	17.461378	0.588757	58.87566
	216	31.378	27.221	4.157	14.898799	0.510653	51.06533
	288	30.537	26.235	4.302	11.563862	0.504663	50.46632
	360	31.692	27.146	4.546	9.7757911	0.48288	48.28802
	432	32.53	27.886	4.644	8.3221099	0.481581	48.15807
	504	32.47	27.613	4.857	7.4604075	0.465853	46.58529

Table 4: Corrosion behaviour of steel sample in in 1.0M H_2SO_4 solution in the presence of formulated inhibitor of *Heliotropium indicum* (HI) at varying immersion time

Conc. (ppm)	Time (Hrs)	Initial W. (W_1)	Final W. (W_2)	ΔW (g)	C.R (mmpy)	I. E. (%)	Θ
100ppm HI	72	30.95	28.272	2.678	28.79407	0.543549	54.35487
	144	31.378	27.201	4.177	22.455719	0.471132	47.11319
	216	31.477	26.588	4.889	17.522306	0.424485	42.4485
	288	30.703	25.559	5.144	13.827175	0.407714	40.77145
	360	30.164	24.823	5.341	11.485372	0.392447	39.24468
	432	32.518	27.014	5.504	9.8632414	0.385577	38.55771
	504	32.338	26.55	5.788	8.8904342	0.363466	36.34664
200ppm HI	72	30.386	27.952	2.434	26.170563	0.585137	58.51372
	144	31.094	27.369	3.725	20.025749	0.528362	52.83616
	216	31.234	26.643	4.591	16.454266	0.459564	45.95644
	288	31.774	26.858	4.916	13.214306	0.433967	43.39666
	360	31.025	25.93	5.095	10.95637	0.42043	42.043
	432	30.772	25.56	5.212	9.3399735	0.418174	41.81737
	504	30.895	25.512	5.383	8.2683495	0.408006	40.80062
300ppm HI	72	31.66	29.511	2.149	23.10622	0.633714	63.3714
	144	30.645	26.958	3.687	19.82146	0.533173	53.3173
	216	30.083	25.799	4.284	15.35397	0.495703	49.57034
	288	32.078	27.453	4.625	12.432093	0.467473	46.74727
	360	32.328	27.497	4.831	10.38866	0.450461	45.04607
	432	31.116	26.112	5.004	8.9672347	0.441393	44.13932
	504	32.199	27.068	5.131	7.8812746	0.43572	43.57198
400ppm HI	72	31.218	29.232	1.986	21.353631	0.661497	66.14965
	144	31.707	28.156	3.551	19.090318	0.550393	55.03925
	216	31.687	27.548	4.139	14.834286	0.512772	51.27722
	288	31.203	26.621	4.582	12.316508	0.472424	47.24237
	360	31.422	26.726	4.696	10.098354	0.465817	46.58173
	432	31.315	26.432	4.883	8.7504011	0.454901	45.49006
	504	31.484	26.467	5.017	7.7061693	0.448257	44.82569
500ppm HI	72	31.459	29.672	1.787	19.213967	0.695415	69.5415
	144	31.463	28.347	3.116	16.751741	0.60547	60.54697
	216	32.361	28.488	3.873	13.880935	0.544085	54.40848
	288	31.018	26.907	4.111	11.05045	0.526655	52.66552
	360	30.164	25.89	4.274	9.190878	0.513821	51.3821
	432	31.022	26.548	4.474	8.0174677	0.500558	50.05582
	504	31.158	26.525	4.633	7.116341	0.490487	49.04872

Table 5: Corrosion behaviour of steel sample in in 1.0M H_2SO_4solution in different concentration of the standard inhibitor (Shell Ensis; SE) at varying immersion time

Concentration (ppm)	**Time** (Hrs)	**Initial W.** (W_1)	**Final W.** (W_2)	**ΔW** (g)	**C.R** (mmpy)	**I. E.** (%)	**Θ**
100ppm SE	72	31.996	29.142	2.854	30.686436	0.51355	51.35504
	144	31.771	27.234	4.537	24.391094	0.425551	42.55508
	216	31.134	25.971	5.163	18.50433	0.392231	39.22307
	288	30.862	25.525	5.337	14.345963	0.385492	38.54922
	360	30.484	25.081	5.403	11.618698	0.385394	38.53942
	432	31.434	25.792	5.642	10.110539	0.370172	37.01719
	504	31.648	25.776	5.872	9.0194591	0.354229	35.42285
200ppm SE	72	30.919	28.302	2.617	28.138193	0.553946	55.39458
	144	31.506	27.164	4.342	23.342766	0.450241	45.02406
	216	31.178	26.334	4.844	17.361025	0.429782	42.97822
	288	31.958	26.887	5.071	13.630949	0.41612	41.61197
	360	31.697	26.43	5.267	11.326241	0.400865	40.08645
	432	31.451	26.16	5.291	9.4815426	0.409355	40.93548
	504	31.806	26.347	5.459	8.3850864	0.399648	39.96481
300ppm SE	72	31.01	28.581	2.429	26.116802	0.585989	58.59894
	144	31.298	27.135	4.163	22.380455	0.472905	47.29045
	216	30.255	25.538	4.717	16.905854	0.444732	44.47322
	288	32.208	27.202	5.006	13.456228	0.423604	42.36039
	360	30.832	25.635	5.197	11.175712	0.408827	40.88272
	432	30.873	25.597	5.276	9.4546624	0.411029	41.10292
	504	31.44	25.854	5.586	8.5801598	0.385681	38.56813
400ppm SE	72	31.103	28.869	2.234	24.020147	0.619226	61.92262
	144	31.255	27.397	3.858	20.740762	0.511522	51.15219
	216	32.274	27.937	4.337	15.543924	0.489464	48.94644
	288	30.243	25.687	4.556	12.246619	0.475417	47.54174
	360	30.984	26.159	4.825	10.375757	0.451143	45.11432
	432	30.973	25.939	5.034	9.0209951	0.438044	43.80442
	504	31.73	26.743	4.987	7.660089	0.451556	45.15561
500ppm SE	72	31.761	29.638	2.123	22.826666	0.638146	63.81456
	144	31.518	27.802	3.716	19.977365	0.529501	52.95011
	216	31.345	27.188	4.157	14.898799	0.510653	51.06533
	288	31.404	27.006	4.398	11.821912	0.49361	49.36097
	360	30.867	26.171	4.696	10.098354	0.465817	46.58173
	432	31.74	26.918	4.822	8.6410883	0.46171	46.17102
	504	31.37	26.434	4.936	7.5817524	0.457165	45.71649

Table 6: Corrosion behaviour of steel sample in 1.0M HCl solution in the presence of formulated inhibitor of *Chrysophyllum albidium* (CA) at varying immersion time

Conc. (ppm)	Time (Hrs)	Initial W. (W_1)	Final W. (W_2)	ΔW (g)	C.R (mmpy)	I. E. (%)	Θ
100ppm CA	72	31.616	31.196	0.42	4.5158736	0.525424	52.54237
	144	32.041	31.503	0.538	2.8923095	0.50139	50.13902
	216	30.572	29.818	0.754	2.7023561	0.431373	43.13725
	288	31.143	30.167	0.976	2.6235075	0.420083	42.00832
	360	31.779	30.562	1.217	2.6170563	0.408936	40.89364
	432	32.753	31.332	1.421	2.5464509	0.386177	38.61771
	504	32.555	31.092	1.463	2.2471847	0.403587	40.35874
200ppm CA	72	30.407	30.086	0.321	3.4514177	0.637288	63.72881
	144	30.624	30.157	0.467	2.5106107	0.567192	56.71918
	216	30.86	30.196	0.664	2.3797937	0.499246	49.92459
	288	30.672	29.813	0.859	2.3090092	0.489602	48.96019
	360	30.641	29.579	1.062	2.2837418	0.484216	48.42156
	432	31.081	29.869	1.212	2.1719202	0.476458	47.64579
	504	32.863	31.574	1.289	1.9799187	0.474521	47.4521
300ppm CA	72	31.175	30.903	0.272	2.9245658	0.692655	69.26554
	144	31.177	30.781	0.396	2.1289118	0.632994	63.29935
	216	32.753	32.176	0.577	2.0679834	0.564857	56.48567
	288	30.953	30.193	0.76	2.0428952	0.548425	54.84254
	360	32.064	31.152	0.912	1.9611794	0.557067	55.70665
	432	31.966	30.884	1.082	1.9389584	0.532613	53.26134
	504	31.941	30.734	1.207	1.8539658	0.507949	50.79494
400ppm CA	72	32.941	32.732	0.209	2.2471847	0.763842	76.38418
	144	31.088	30.724	0.364	1.9568786	0.662651	66.26506
	216	31.395	30.844	0.551	1.9747987	0.584465	58.44646
	288	31.592	30.863	0.729	1.9595666	0.566845	56.68449
	360	32.59	31.738	0.852	1.8321544	0.586207	58.62069
	432	32.563	31.562	1.001	1.7938053	0.567603	56.76026
	504	31.582	30.417	1.165	1.7894533	0.525071	52.50713
500ppm CA	72	31.182	31.049	0.133	1.4300266	0.849718	84.97175
	144	31.807	31.585	0.222	1.5075548	0.74011	74.01102
	216	30.434	30.059	0.375	1.34401	0.717195	71.71946
	288	31.267	30.748	0.519	1.3950824	0.691622	69.16221
	360	31.045	30.386	0.659	1.4171241	0.679942	67.99417
	432	31.182	30.358	0.824	1.476619	0.64406	64.40605
	504	30.693	29.667	1.026	1.5759477	0.581737	58.17366

Table 7: Corrosion behaviour of steel sample in 1.0M HCl solution in the presence of formulated inhibitor of *Heliotropium indicum* (HI) at varying immersion time

Conc. (ppm)	**Time** (Hrs)	**Initial W.** (W_1)	**Final W.** (W_2)	**ΔW** (g)	**C.R** (mmpy)	**I. E.** (%)	Θ
100ppm HI	72	30.574	30.23	0.344	3.6987155	0.611299	61.12994
	144	30.114	29.669	0.445	2.3923378	0.587581	58.75811
	216	31.198	30.537	0.661	2.3690416	0.501508	50.15083
	288	30.822	29.966	0.856	2.3009451	0.491384	49.13844
	360	30.842	29.781	1.061	2.2815914	0.484701	48.47013
	432	32.391	31.169	1.222	2.1898403	0.472138	47.21382
	504	32.351	31.008	1.343	2.0628634	0.452507	45.25071
200ppm HI	72	31.088	30.782	0.306	3.2901365	0.654237	65.42373
	144	31.814	31.378	0.436	2.3439534	0.595922	59.59222
	216	32.18	31.534	0.646	2.3152812	0.512821	51.28205
	288	31.362	30.561	0.801	2.153104	0.524064	52.40642
	360	31.609	30.608	1.001	2.1525664	0.513842	51.38417
	432	31.075	29.922	1.153	2.0661914	0.501944	50.19438
	504	32.562	31.268	1.294	1.9875988	0.472483	47.24827
300ppm HI	72	30.168	29.893	0.275	2.956822	0.689266	68.92655
	144	32.764	32.345	0.419	2.2525608	0.611677	61.16775
	216	31.899	31.313	0.586	2.1002396	0.558069	55.80694
	288	32.399	31.626	0.773	2.0778395	0.540701	54.07011
	360	31.654	30.686	0.968	2.0816027	0.529869	52.98689
	432	31.043	29.939	1.104	1.9783827	0.52311	52.31102
	504	30.95	29.767	1.183	1.8171015	0.517733	51.77334
400ppm HI	72	32.476	32.253	0.223	2.3977138	0.748023	74.80226
	144	30.882	30.483	0.399	2.14504	0.630213	63.02132
	216	30.927	30.361	0.566	2.0285591	0.573152	57.31523
	288	31.367	30.613	0.754	2.0267671	0.55199	55.19905
	360	31.516	30.585	0.931	2.0020373	0.547839	54.78388
	432	30.98	29.907	1.073	1.9228303	0.536501	53.65011
	504	31.822	30.646	1.176	1.8063494	0.520587	52.0587
500ppm HI	72	31.154	30.961	0.193	2.0751514	0.781921	78.19209
	144	30.361	30.062	0.299	2.0304454	0.649968	64.99683
	216	31.085	30.552	0.533	1.9102862	0.598039	59.80392
	288	31.088	30.404	0.684	1.8386057	0.593583	59.35829
	360	30.133	29.287	0.846	1.8192519	0.589121	58.91209
	432	30.637	29.624	1.013	1.8153095	0.562419	56.2419
	504	32.688	31.595	1.093	1.6788605	0.554423	55.44232

Table 8: Corrosion behaviour of steel sample in 1.0M HCl solution in different concentration of the standard inhibitor (Shell Ensis; SE) at varying immersion time

Conc. (ppm)	**Time** (Hrs)	**Initial** W. (W_1)	**Final** W. (W_2)	**ΔW** (g)	**C.R** (mmpy)	**I. E.** (%)	Θ
100ppm SE	72	31.273	30.874	0.399	4.29008	0.549153	54.91525
	144	30.895	30.364	0.531	2.854677	0.507878	50.78777
	216	31.365	30.664	0.701	2.512403	0.471342	47.13424
	288	30.955	30.037	0.918	2.467602	0.454545	45.45455
	360	31.787	30.644	1.143	2.457925	0.444876	44.48762
	432	30.87	29.554	1.316	2.35829	0.431533	43.15335
	504	31.684	30.268	1.416	2.174992	0.422748	42.27477
200ppm SE	72	30.805	30.458	0.347	3.730972	0.60791	60.79096
	144	31.221	30.721	0.5	2.68802	0.536608	53.6608
	216	32.74	32.101	0.639	2.290193	0.5181	51.80995
	288	31.63	30.787	0.843	2.266001	0.499109	49.91087
	360	31.801	30.75	1.051	2.260087	0.489558	48.9558
	432	31.208	29.992	1.216	2.179088	0.47473	47.473
	504	31.987	30.651	1.336	2.052111	0.455361	45.53608
300ppm SE	72	31.261	30.965	0.296	3.182616	0.665537	66.55367
	144	31.517	31.092	0.425	2.284817	0.606117	60.61168
	216	30.336	29.745	0.591	2.11816	0.554299	55.42986
	288	30.794	30.011	0.783	2.10472	0.534759	53.47594
	360	31.424	30.469	0.955	2.053647	0.536183	53.61826
	432	30.905	29.788	1.117	2.001679	0.517495	51.74946
	504	32.004	30.792	1.212	1.861646	0.505911	50.59111
400ppm SE	72	30.141	29.898	0.243	2.612755	0.725424	72.54237
	144	32.341	31.943	0.398	2.139664	0.63114	63.11399
	216	31.383	30.849	0.534	1.91387	0.597285	59.72851
	288	31.877	31.168	0.709	1.905806	0.578728	57.87285
	360	30.689	29.832	0.857	1.842907	0.583779	58.37785
	432	30.508	29.512	0.996	1.784845	0.569762	56.97624
	504	31.214	30.077	1.137	1.746445	0.536486	53.64859
500ppm SE	72	31.917	31.721	0.196	2.107408	0.778531	77.85311
	144	31.327	31.028	0.299	2.030445	0.649968	64.99683
	216	31.408	30.913	0.495	1.774093	0.626697	62.66968
	288	31.24	30.582	0.658	1.768717	0.609031	60.90315
	360	32.66	31.849	0.811	1.743987	0.606119	60.61195
	432	30.901	29.864	1.037	1.858318	0.552052	55.20518
	504	30.978	29.836	1.142	1.754125	0.534448	53.44476

Table 9: Corrosion behaviour of steel sample in 1.0M H_2SO_4 solution in the presence of formulated inhibitor of *Chrysophyllum albidium* (CA) at varying temperature (303 -33K).

Conc.	Initial W. (W_1)	Final W. (W_2)	ΔW (g)	C.R (mmpy)	Θ	I. E (%)	Temp. (K)
Blank	31.364	31.332	0.032	24.77279			303
100ppm	30.931	32.362	0.023	17.80544	0.28125	28.125	303
200ppm	31.404	32.574	0.018	13.9347	0.217391	21.73913	303
300ppm	31.337	30.876	0.016	12.3864	0.5	50	303
400ppm	33.336	30.823	0.014	10.8381	0.5625	56.25	303
500ppm	31.845	31.536	0.012	9.289797	0.625	62.5	303
Blank	32.23	32.834	0.074	57.28708			313
100ppm	34.278	31.734	0.048	37.15919	0.351351	35.13514	313
200ppm	32.009	32.762	0.036	27.86939	0.513514	51.35135	313
300ppm	31.271	31.545	0.031	23.99864	0.581081	58.10811	313
400ppm	32.46	31.439	0.029	22.45034	0.608108	60.81081	313
500ppm	32.063	33.698	0.025	19.35374	0.662162	66.21622	313
Blank	32.807	31.866	0.184	142.4436			323
100ppm	31.731	32.744	0.089	68.89933	0.516304	51.63043	323
200ppm	32.769	31.931	0.077	59.60953	0.581522	58.15217	323
300ppm	31.684	32.734	0.071	54.96463	0.61413	61.41304	323
400ppm	31.529	31.701	0.063	48.77143	0.657609	65.76087	323
500ppm	32.191	32.281	0.059	45.67484	0.679348	67.93478	323
Blank	32.309	31.354	0.478	370.0436			333
100ppm	31.651	31.922	0.184	142.4436	0.615063	61.50628	333
200ppm	32.063	32.247	0.166	128.5089	0.65272	65.27197	333
300ppm	31.339	33.468	0.162	125.4123	0.661088	66.10879	333
400ppm	31.713	32.344	0.156	120.7674	0.67364	67.36402	333
500ppm	32.344	31.481	0.15	116.1225	0.686192	68.61925	333

Table 10: Corrosion behaviour of steel sample in 1.0M H_2SO_4 solution in the presence of formulated inhibitor of *Heliotropium indicum* (HI) at varying temperature (303 -33K).

Conc.	Initial W.(W_1)	Final W. (W_2)	ΔW (g)	C.R (mmpy)	Θ	I. E (%)	Temp (K)
Blank	31.364	31.332	0.032	24.77279	0		303
100ppm	30.605	30.583	0.022	17.03129	0.3125	31.25	303
200ppm	31.336	31.316	0.02	15.483	0.375	37.5	303
300ppm	32.161	32.144	0.017	13.16055	0.46875	46.875	303
400ppm	31.254	31.24	0.014	10.8381	0.5625	56.25	303
500ppm	30.065	30.053	0.012	9.289797	0.625	62.5	303
Blank	32.23	32.156	0.074	57.28708			313
100ppm	32.238	32.19	0.048	37.15919	0.351351	35.13514	313
200ppm	32.113	32.072	0.041	31.74014	0.445946	44.59459	313
300ppm	30.905	30.87	0.035	27.09524	0.527027	52.7027	313
400ppm	32.249	32.219	0.03	23.22449	0.594595	59.45946	313
500ppm	32.418	32.392	0.026	20.12789	0.648649	64.86486	313
Blank	32.807	32.623	0.184	142.4436			323
100ppm	32.597	32.486	0.111	85.93062	0.396739	39.67391	323
200ppm	32.767	32.675	0.092	71.22178	0.5	50	323
300ppm	31.684	31.608	0.076	58.83538	0.586957	58.69565	323
400ppm	30.685	30.616	0.069	53.41633	0.625	62.5	323
500ppm	31.552	31.491	0.061	47.22314	0.668478	66.84783	323
Blank	32.309	31.831	0.478	370.0436			333
100ppm	32.05	31.855	0.195	150.9592	0.59205	59.20502	333
200ppm	31.562	31.405	0.157	121.5415	0.671548	67.15481	333
300ppm	32.797	32.656	0.141	109.1551	0.705021	70.50209	333
400ppm	31.767	31.63	0.137	106.0585	0.713389	71.33891	333
500ppm	33.943	33.81	0.133	102.9619	0.721757	72.17573	333

Table 11: Corrosion behaviour of steel sample in 1.0M H_2SO_4 solution in different concentration of the standard inhibitor (Shell Ensis; SE) at varying temperature (303 - 33K).

Conc.	Initial W. (W_1)	Final W. (W_2)	ΔW (g)	C.R (mmpy)	Θ	I. E (%)	Temp (K)
Blank	31.364	31.332	0.032	24.77279	0		303
100ppm	31.728	31.704	0.024	18.57959	0.25	25	303
200ppm	32.682	32.661	0.021	16.25714	0.34375	34.375	303
300ppm	31.603	31.584	0.019	14.70885	0.40625	40.625	303
400ppm	32.546	32.529	0.017	13.16055	0.46875	46.875	303
500ppm	31.929	31.913	0.016	12.3864	0.5	50	303
Blank	32.23	32.156	0.074	57.28708			313
100ppm	31.065	31.014	0.051	39.48164	0.310811	31.08108	313
200ppm	31.889	31.846	0.043	33.28844	0.418919	41.89189	313
300ppm	32.237	32.198	0.039	30.19184	0.472973	47.2973	313
400ppm	30.731	30.696	0.035	27.09524	0.527027	52.7027	313
500ppm	30.533	30.502	0.031	23.99864	0.581081	58.10811	313
Blank	32.807	32.623	0.184	142.4436			323
100ppm	32.154	32.039	0.115	89.02722	0.375	37.5	323
200ppm	32.082	31.984	0.098	75.86668	0.467391	46.73913	323
300ppm	32.588	32.499	0.089	68.89933	0.516304	51.63043	323
400ppm	32.6	32.522	0.078	60.38368	0.576087	57.6087	323
500ppm	32.251	32.181	0.07	54.19048	0.619565	61.95652	323
Blank	32.309	31.831	0.478	370.0436			333
100ppm	30.089	29.864	0.225	174.1837	0.529289	52.92887	333
200ppm	30.349	30.141	0.208	161.0232	0.564854	56.48536	333
300ppm	31.602	31.407	0.195	150.9592	0.59205	59.20502	333
400ppm	30.869	30.682	0.187	144.766	0.608787	60.87866	333
500ppm	32.363	32.179	0.184	142.4436	0.615063	61.50628	333

Table 12: Corrosion behaviour of steel sample in 1.0M HCl solution in the presence of formulated inhibitor of *Chrysophyllum albidium* (CA) at varying temperature (303 -33K).

Conc.	Initial (W_1)	Final W.(W_2)	ΔW (g)	C.R (mmpy)	Θ	I. E (%)	Temp (K)
Blank	31.779	31.756	0.023	17.80544	0		303
100ppm	32.377	32.362	0.015	11.61225	0.347826	34.78261	303
200ppm	32.586	32.574	0.012	9.289797	0.478261	47.82609	303
300ppm	30.883	30.876	0.007	5.419048	0.695652	69.56522	303
400ppm	30.829	30.823	0.006	4.644899	0.73913	73.91304	303
500ppm	31.541	31.536	0.005	3.870749	0.782609	78.26087	303
Blank	32.886	32.834	0.052	40.25579			313
100ppm	31.757	31.734	0.023	17.80544	0.557692	55.76923	313
200ppm	32.782	32.762	0.02	15.483	0.615385	61.53846	313
300ppm	31.562	31.545	0.017	13.16055	0.673077	67.30769	313
400ppm	31.453	31.439	0.014	10.8381	0.730769	73.07692	313
500ppm	33.709	33.698	0.011	8.515647	0.788462	78.84615	313
Blank	31.979	31.862	0.117	90.57552			323
100ppm	32.791	32.744	0.047	36.38504	0.598291	59.82906	323
200ppm	31.972	31.931	0.041	31.74014	0.649573	64.95726	323
300ppm	32.769	32.734	0.035	27.09524	0.700855	70.08547	323
400ppm	31.729	31.701	0.028	21.67619	0.760684	76.06838	323
500ppm	32.304	32.281	0.023	17.80544	0.803419	80.34188	323
Blank	31.653	31.354	0.299	231.4708			333
100ppm	32.014	31.922	0.092	71.22178	0.692308	69.23077	333
200ppm	32.332	32.247	0.085	65.80273	0.715719	71.57191	333
300ppm	33.54	33.468	0.072	55.73878	0.759197	75.91973	333
400ppm	32.406	32.345	0.061	47.22314	0.795987	79.59866	333
500ppm	31.532	31.484	0.048	37.15919	0.839465	83.94649	333

Table 13: Corrosion behaviour of steel sample in 1.0M HCl solution in the presence of formulated inhibitor of *Heliotropium indicum* (HI) at varying temperature (303 -33K).

Conc.	Initial (W_1)	Final W.(W_2)	ΔW (g)	C.R (mmpy)	Θ	I. E (%)	Temp (K)
Blank	31.779	31.756	0.023	17.80544	0		303
100ppm	32.72	32.707	0.013	10.06395	0.434783	43.47826	303
200ppm	32.25	32.239	0.011	8.515647	0.521739	52.17391	303
300ppm	31.872	31.862	0.01	7.741498	0.565217	56.52174	303
400ppm	33.051	33.042	0.009	6.967348	0.608696	60.86957	303
500ppm	32.515	32.507	0.008	6.193198	0.652174	65.21739	303
Blank	32.886	32.834	0.052	40.25579			313
100ppm	33.542	33.519	0.023	17.80544	0.557692	55.76923	313
200ppm	31.785	31.765	0.02	15.483	0.615385	61.53846	313
300ppm	33.548	33.532	0.016	12.3864	0.692308	69.23077	313
400ppm	31.644	31.63	0.014	10.8381	0.730769	73.07692	313
500ppm	34.608	34.596	0.012	9.289797	0.769231	76.92308	313
Blank	31.979	31.862	0.117	90.57552			323
100ppm	31.665	31.623	0.042	32.51429	0.641026	64.10256	323
200ppm	32.7	32.666	0.034	26.32109	0.709402	70.94017	323
300ppm	31.609	31.581	0.028	21.67619	0.760684	76.06838	323
400ppm	31.16	31.135	0.025	19.35374	0.786325	78.63248	323
500ppm	31.049	31.026	0.023	17.80544	0.803419	80.34188	323
Blank	31.653	31.354	0.299	231.4708			333
100ppm	33.364	33.272	0.092	71.22178	0.692308	69.23077	333
200ppm	31.965	31.897	0.068	52.64218	0.772575	77.25753	333
300ppm	32.076	32.016	0.06	46.44899	0.799331	79.93311	333
400ppm	33.879	33.82	0.059	45.67484	0.802676	80.26756	333
500ppm	31.471	31.42	0.051	39.48164	0.829431	82.94314	333

Table 14: Corrosion behaviour of steel sample in 1.0M HClsolution in different concentration of the standard inhibitor (Shell Ensis; SE) at varying temperature (303 - 33K).

Conc.	Initial (W_1)	Final W. (W_2)	ΔW (g)	C.R (mmpy)	Θ	I. E (%)	Temp (K)
Blank	31.779	31.756	0.023	17.80544	0		303
100ppm	32.796	32.783	0.013	10.06395	0.434783	43.47826	303
200ppm	31.536	31.523	0.013	10.06395	0.434783	43.47826	303
300ppm	32.9	32.888	0.012	9.289797	0.478261	47.82609	303
400ppm	31.844	31.834	0.01	7.741498	0.565217	56.52174	303
500ppm	31.361	31.353	0.008	6.193198	0.652174	65.21739	303
Blank	32.886	32.834	0.052	40.25579			313
100ppm	32.467	32.441	0.026	20.12789	0.5	50	313
200ppm	32.649	32.627	0.022	17.03129	0.576923	57.69231	313
300ppm	33.384	33.364	0.02	15.483	0.615385	61.53846	313
400ppm	32.048	32.031	0.017	13.16055	0.673077	67.30769	313
500ppm	31.631	31.618	0.013	10.06395	0.75	75	313
Blank	31.979	31.862	0.117	90.57552			323
100ppm	32.879	32.837	0.042	32.51429	0.641026	64.10256	323
200ppm	31.528	31.494	0.034	26.32109	0.709402	70.94017	323
300ppm	32.283	32.251	0.032	24.77279	0.726496	72.64957	323
400ppm	31.625	31.597	0.028	21.67619	0.760684	76.06838	323
500ppm	33.629	33.603	0.026	20.12789	0.777778	77.77778	323
Blank	31.653	31.354	0.299	231.4708			333
100ppm	33.374	33.285	0.089	68.89933	0.702341	70.23411	333
200ppm	32.352	32.269	0.083	64.25443	0.722408	72.2408	333
300ppm	31.304	31.225	0.079	61.15783	0.735786	73.5786	333
400ppm	31.797	31.721	0.076	58.83538	0.745819	74.58194	333
500ppm	31.734	31.675	0.059	45.67484	0.802676	80.26756	333

Appendix IV: - The UV-VIS spectrum of plant extracts

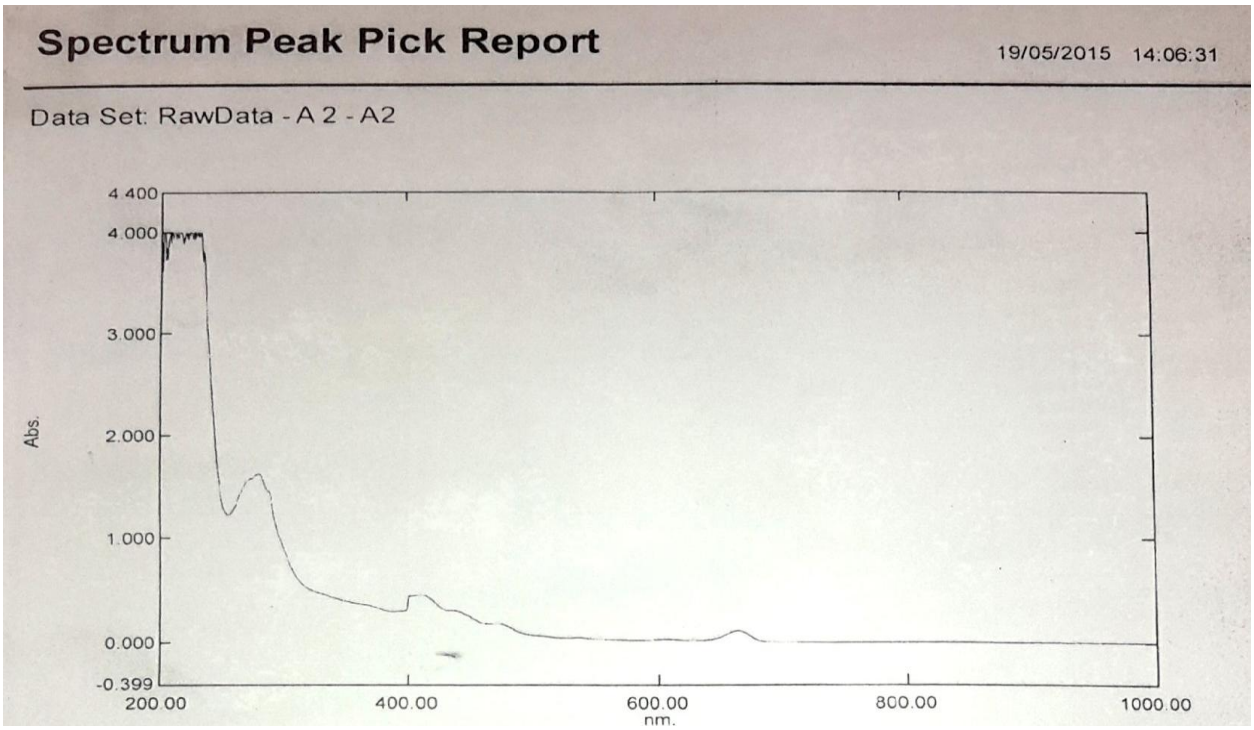


Figure 1: The UV-VIS spectrum of sample A

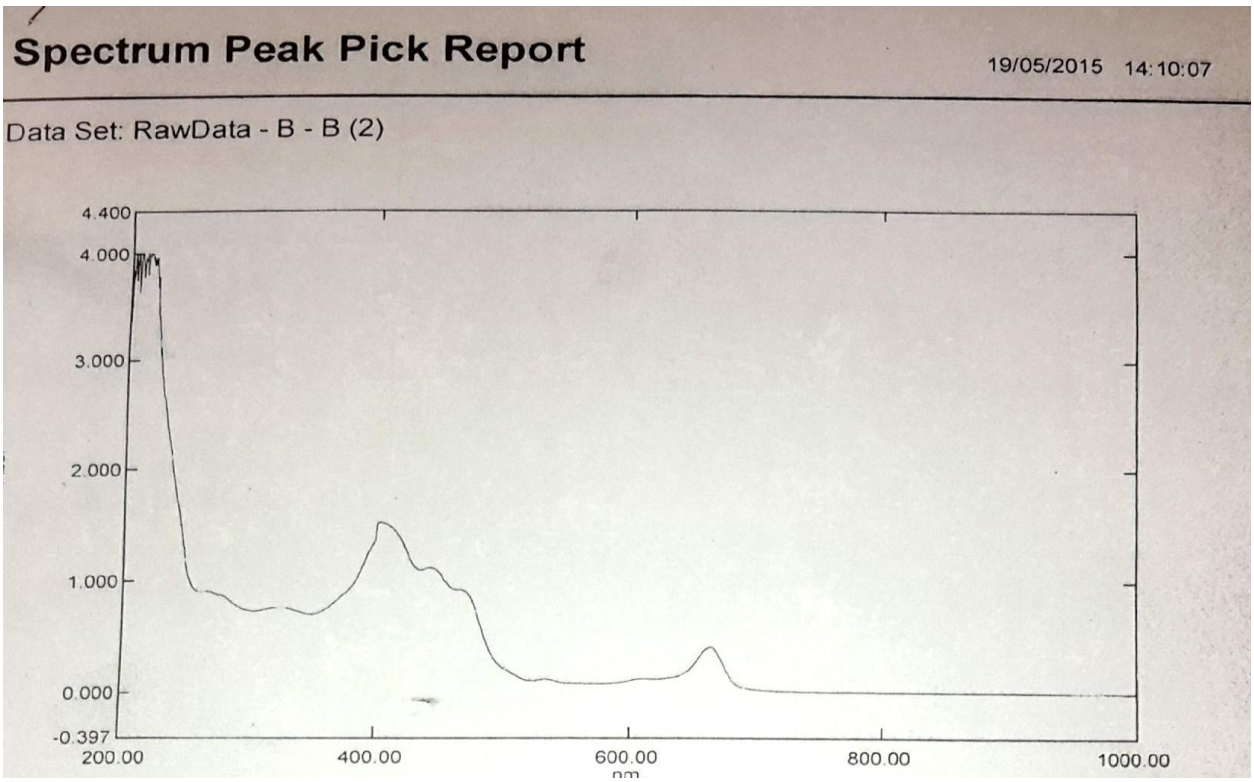


Figure 2: The UV-VIS spectrum of sample B

Appendix V: - SEM image of as-received medium carbon low alloy steel sample

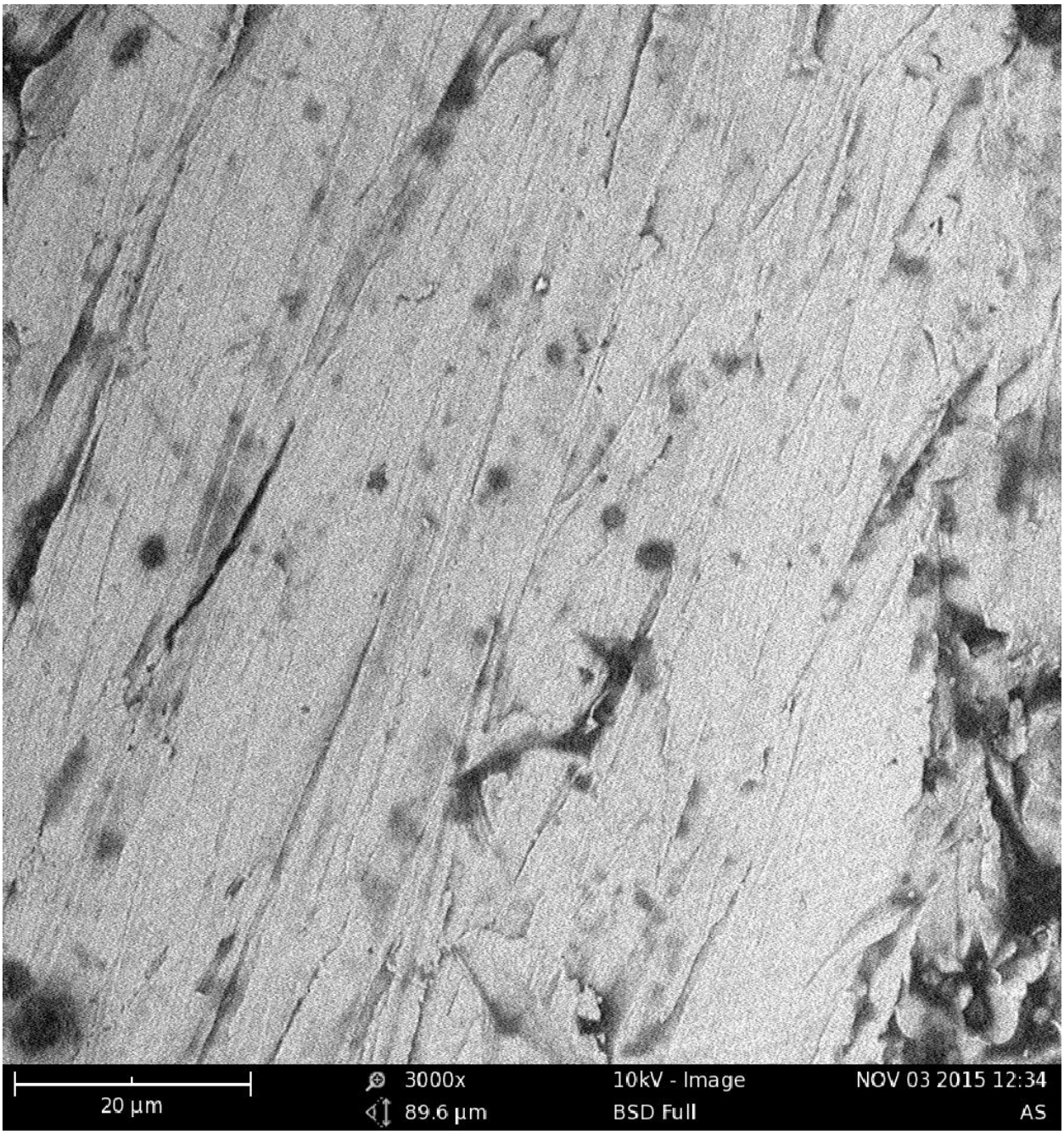


Plate 1: SEM image of as-received medium carbon low alloy steel

Appendix VI: - Specimens Used for Tensile and Impact Mechanical Tests

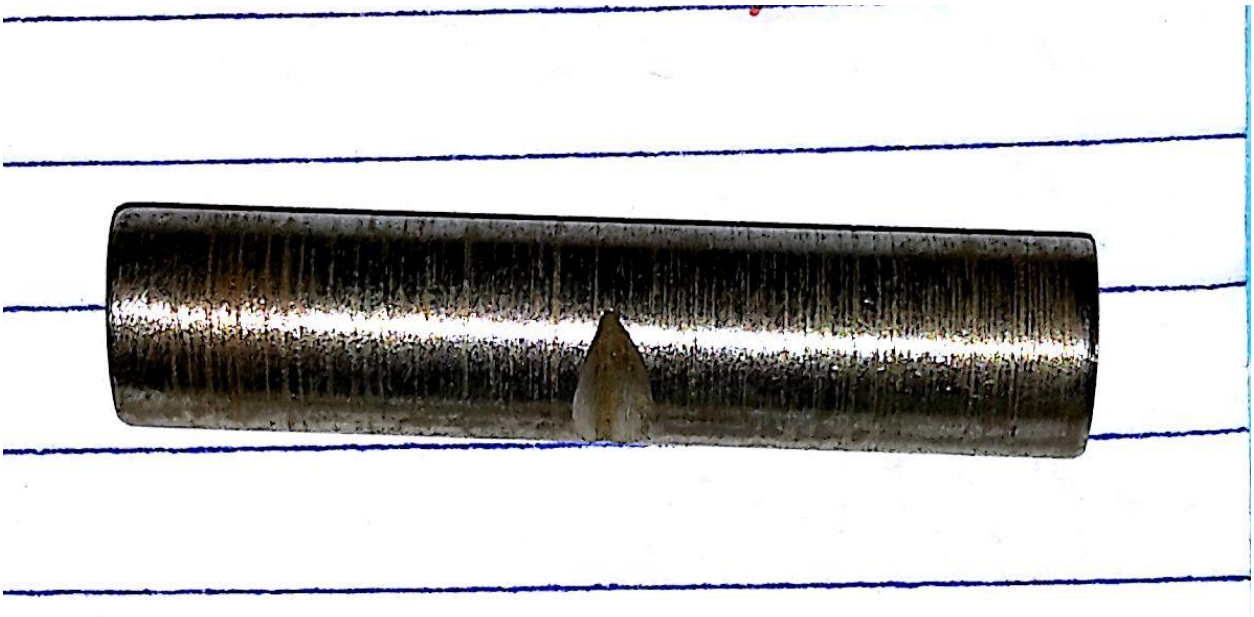


Fig. 3: Specimen used for Impact Mechanical Test

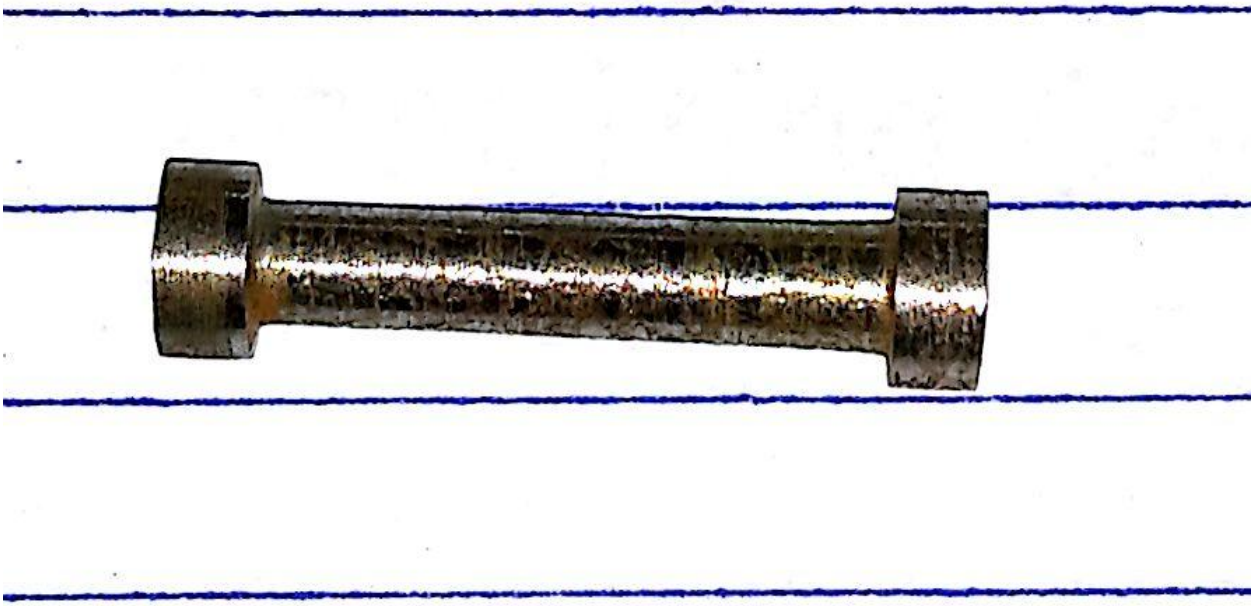


Fig. 4: Specimen used for Tensile Mechanical Test

Appendix VII: Equipment Used and Location

Process	Activity/Study	Equipment/instrument used	Location
Coupons preparation	Elemental composition and Microstructural Examination	Emission Optical spectrometer and Nikon Metallurgical Microscope	Abuja Steel Mills, Suleja and Nigerian Foundries, Ilupeju Lagos
	Mechanical Cutting and surface finishing	Hack saw, saw blade, files and emery paper	Acquired
	Coupons polishingand conditioning	Polishingmachine and analytical mass balance	MME, Abu, Zaria
Bio-extraction and inhibitors preparation	Pulverization, sieve sizing and extraction	Lab. Size Mechanical grinder and bench vice	Mech. Engineering, Abu, zaria
		Digital mass balance, soxhlet extractor, and water bath	Pharmacognosy, Abu, Zaria
		Mesh sieve, Filtration funnels100 mL glassware round containers,and Aluminum foils paper	Acquired
		Water bath	Pharmacognosy, Abu, Zaria
Corrosion tests	Weight loss; kinectic and thermodynamics techniques; Linear Polarization Resistance Studies	1L glassware and 150 mL plastics containers	Acquired
		Beakers, Digital mass balance and water bath	Chemistry, Abu, Zaria
		AC Autolab Potentiostat and electrochemical cell	MME, Abu, Zaria
Proximate Analysis and Quantitative Phytochemical screening	Proximate analysis and Quantitative screening	Filterpapers	Acquired
		Digital weighing balance, desiccator, water bath, incinerator, Crucible, Muffle furnance,AAS and soxhlet extractor	IAR, Samaru
Absorption Mechanism and Chemistry studies	Surface and chemistry studies, Surface analysis	UV Spectrophotometry	OAU, Ile-Ife
		SEM coupled EDX and Fourier Transform Infrared Spectroscopy	Chemical Engineering and Chemistry department, Abu, Zaria

Process	Activity/Study	Equipment/instrument used	Location
Physico-chemical studies	Viscosity, Solubility, Density, Odour, Colour, pH and Biodegradable tests	KVDV-1 Digital Viscometer	Physics, Abu, Zaria
		Magnetic stirrer, Incubator, digital pH meter and digital weighing balance	Water resources, Abu, Zaria
Mechanical properties	Tensile, Hardness and Impact tests	Computerized Universal and 20kN HounsfieldTensometer	Abuja Steel Mills, Suleja and Mech. Engineering, Abu, Zaria
		Impact tester (120 foot-pound)	Mech. Engineering, Abu, Zaria
		Brooks Universal Hardness machine (CRBD W2.5/187.5)	Nigerian foundries, Ilupeju-Lagos and MME, Abu, Zaria