

## CHAPTER ONE

### 1.0 Background of the study

Corrosion has been around us even before industries came to existence and the need for the prevention or cure has been a major problem. Aggressive acids such as hydrochloric acid are frequently used to remove mild scale and rust from iron and steel in chemical industries (Ibot *et al.*, 2010). These inhibitors were utilized by the industries for their anti-corrosive properties but they cause some adverse effects on the environment. This led to the development of corrosion inhibitors which are environmentally friendly and are called Organic Corrosion Inhibitors (OCI) (Bommersbach *et al.*, 2005). Corrosion Inhibition can be carried out by the use of organic or inorganic approach. The organic approach is also known as Green Corrosion Inhibition. One of the best-known corrosion safety techniques is the corrosion inhibitor (Al-Otaibi *et al.*, 2012). The use of extract of natural product as inhibitor of corrosion was first evidence in 1930 when extracts from *Chelidoniummajus* (Celadine) and other plants were utilized in Sulphuric acid, H<sub>2</sub>SO<sub>4</sub> medium for the first time (Raja *et al.*, 2008).

With this, there is no or minimal amount of pollution caused and it is cost efficient since these are extracts from plants that can be easily isolated. In general, organic compounds with heteroatom having lone pairs of electrons (N, O, S and P), aromatic rings, conjugated systems, and conjugated aliphatic bonds are considered effective corrosion inhibitors (Raja *et al.*, 2008), and pi-electrons, often have ionizable parts which are either hydrophilic or hydrophobic in nature (Aprael *et al.*, 2013). More research and developments are emerging in the study of natural corrosion inhibitors as need for environmental friendly inhibitors are gaining ground. For example, Cr<sub>2</sub>O<sub>3</sub> given its relative insolubility in aqueous environments that span the environmental pH continuum and its adherence to the underlying metal, it may serve as a barrier to corrosion. (Kendig *et al.*, 2004). Hexavalent chromium has shown to induce irrevocable health damage which includes nose, skin irritation, eye and throat but most significantly raises the alarm of lung cancer (Herman *et al.*, 2000). For application in coatings and primers, a comparable universal anti-corrosion compound has yet to be found, so that the need for

chromate substitutes and ways of deployment of corrosion protection spans many industries. Drugs had been studied as corrosion inhibitor at some time (Obot *et al.*, 2009). Over the decades, green chemistry has shown how basic scientific approaches can benefit from the conservation of the human health and that of the environment by combining areas such as polymers (Tao *et al.*, 2011). Awareness to corrosion and the adaptation of fast, appropriate and accurate control measures holds the key in the eradication of corrosion failures. Heterocyclic molecules show essential behavior as anti-corrosion owing to the available of sulfur, oxygen, and nitrogen in their ring structure.

### **1.0.1 Statement of the Problem**

In the time past, hydrochloric acid and chromate compounds were commonly used as inhibitor. Observation It has been observed that they wear the surface of the metal even more and are toxic respectively. In general, they are not environmentally friendly and not well economical. This led to the invention of environmentally friendly and economical inhibitors with green source.

### **1.0.2 Aim and Objectives of the Study**

The aims and objectives of this study include the following:

- i. to prepare inhibitor from plant origin,
- ii. to determine the various bio-molecules present in the inhibitor using GC-MS and FT-IR,
- iii. to examine inhibition efficiency of the prepared inhibitor in acidic medium, and
- iv. to evaluate the effects of contact time, temperature and inhibitor concentration on inhibition efficiency of the prepared inhibitor.

### **1.0.3 Scope of the Study**

This study covers researches into the use of *Musa paradisiacal* leaves extracts as corrosion inhibitor.

### **1.4 Significance of the Study**

This research work is carried out to support the works of many other researchers who are solving the problem of environmental pollution by toxic compounds by using naturally occurring plant source such as; plantain on corrosion inhibitors.

## **1.5 Definition of Terms**

**Corrosion** is a gradual destruction or undermining of a material (metal). Chemically, it is erosion through chemical action, especially oxidation.

**Inhibitor** is any substance capable of stopping or slowing a specific chemical process or reaction (corrosion).

## CHAPTER TWO

### LITERATURE REVIEW

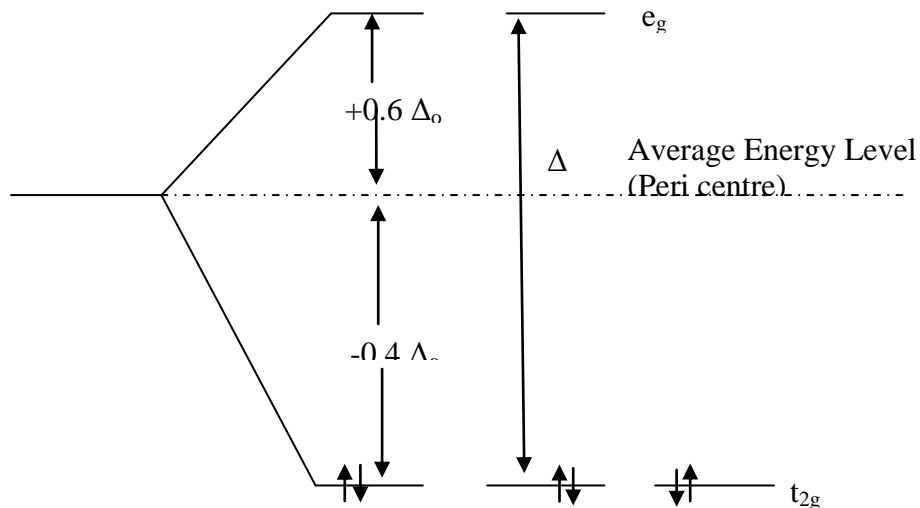
#### 2.0 CORROSION

Corrosion can be defined as an irreversible interfacial reaction of a substance (metals, ceramics and polymers) with its surroundings, resulting in its consumption or dissolution into an environmental component material. Corrosion sometimes but not always, results in damaging effects on the use of the substance concerned. The term corrosion does not exclusively include mechanical or physical processes such as melting and evaporation, abrasion or mechanical processes fracture. Corrosion results in material denudation, devaluation and decay, and this could result in the loss of important material components.

Corrosion of metals and alloys especially in acidic media is a significant industrial issue. Its processes are responsible for numerous losses mainly in the industrial scope. It has a huge economic and environmental impact on all parts of national infrastructure; from highways, buildings, bridges, oil and gas refineries, chemical processing factories, water and waste water treatment plants to entirely all metallic objects in use. In other words, corrosion processes deal with reaction of metals with environmental species.

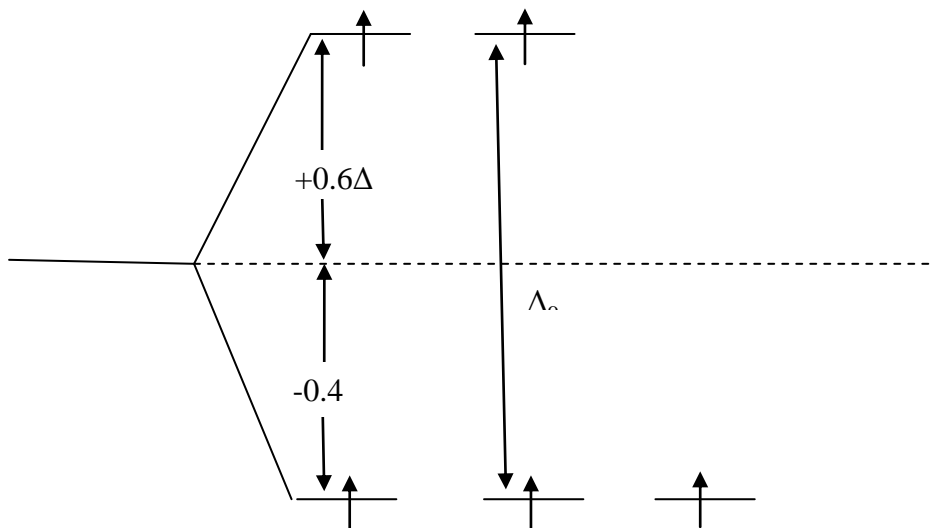
##### 2.0.1 Corrosion Mechanism

Iron, (Fe) is a metal of economic importance with ionic configuration of  $[\text{Ar}] 4s^2 3d^6$ . When iron is exposed to atmosphere, it exists as  $\text{Fe}^{2+}$  due to the loss of two electrons from the 4s orbital which is lower in energy than the 3d orbital to the constituents of the atmosphere to form oxides. The Valence Bond Theory (VBT) and Ligand Field Theory (LFT) can also be used to explain this phenomenon. Upon exposure of iron to acid such as HCl solution, it exist in a form of high spin  $3d^6$  owing to the presence of  $\text{OH}^-$  and  $\text{Cl}^-$  which are weak ligands.. As shown in the Fig. 2.1 below:



**Fig. 2.1:**  $Fe^{2+}$  ion and energy levels of d orbital in octahedral field (Low spin)

The high spin state is a very unstable state, singly filled or fully paired is considered to be stable. Thereby making  $Fe^{2+}$  be oxidized further to  $Fe^{3+}$ , losing one more electron from the 3d orbital ( $t_{2g}$ ) to attain stability. At this point, all the five d orbital [ $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}(t_{2g})$ ,  $d_{x^2-y^2}$  and  $d_{z^2}(e_g)$ ] are singly filled.



**Fig. 2.2:**  $Fe^{3+}$  ion and energy levels of d orbital in octahedral

The electron loss occurred at the anode and then is deposited at the cathode within the same metal. And  $H^+$  from the acid will be reduced to  $H$  atom at the cathode also. Hydrogen molecule is thereby formed and released as gas. But in neutral medium or alkaline, water will be formed as  $H^+$  reacts with

*OH*. As  $Fe^{2+}$  is oxidized to  $Fe^{3+}$ , it detaches from the metal matrix and dissolved in the solution or deposited on the metal surface. This process continues in the presence of acid until the metal is totally worn off.

### 2.0.2 Causes of Corrosion

Corrosion is a natural phenomenon involving the degradation of metal components into their ores e.g. oxides, sulfides, etc. The energy that was once gained during extraction and purification are released during this process. Corrosion is seen as an electrochemical reaction that can appear in several forms, such as chemical corrosion and atmospheric corrosion. Atmospheric corrosion is so common and widespread due to presence of corrosive agents in the atmosphere. The resulting effect of corrosion is rust. Rust is the product dissolving steel after oxygen and moisture have been exposed to the iron particles simultaneously. (e.g. humidity, vapor, and immersion). It is important to note that steel is an alloy of *Fe* and *C*. Carbon is bonded to Iron to reduce corrosion and the formation of steel is a function of *Fe-C* phase present i.e. Ferrite ( $\alpha Fe$ ), Austenite ( $\gamma Fe$ ), Cementite ( $Fe_3C$ ), Pearlite ( $\alpha Fe + Fe_3C$ ). The bonding of *C* with *Fe* in Cementite made the  $3d^6$  electrons of *Fe* to remain in  $t_{2g}$  that is low spin.

Consequently, the four electrons of the carbon are made readily available to the  $e_g$  orbital for bonding. The ferrite regions are the most reactive site and tend to corrode easily. The iron particles become oxidized in water when they are lost to the water's acidic electrolytes, resulting in the formation of  $Fe^+$ . The formed *Fe* ion migrates to another area of the steel called the cathode part. The hydroxyl ions formed from reaction of the electrons with oxygen react with the  $Fe^+$  to form hydrous iron oxide ( $FeOH$ ), also known as rust. The area not affected by rust (where the affected iron particles were) is known as corrosion pit and the affected part (where the electrons are now) of the steel is the rust.

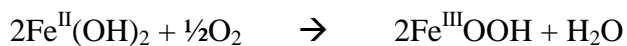
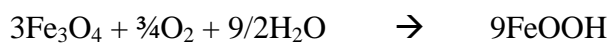
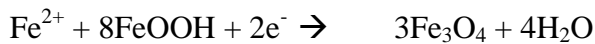
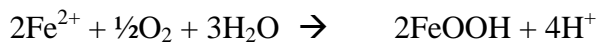
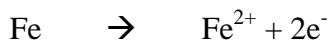
In electronic process measurement, the factors that can cause circuit board corrosion in industrial environment are humidity, temperature and gaseous contaminants. The most harmful are gaseous

contaminants. They are caused primarily by burnt fuel, factories domestic and commercial buildings, etc. Gaseous pollutants are mainly sulfur dioxide ( $SO_2$ ), ozone ( $O_3$ ), and nitrogen dioxide ( $NO_2$ ). The reaction is initialized by water or moisture in the atmosphere in the presence of atmospheric oxygen. The reaction as shown below indicates the corrosion of iron material.

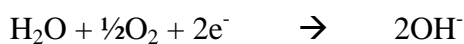
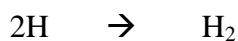
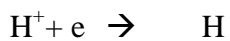
Anodic reaction shows the exposed part of the metal which reacts with water to give a hydroxide and liberation of  $H_2$  gas.

Cathodic reaction shows the reduction of the metal matrix. The reaction continues and is seen to be simultaneous (equation 1-12) and happen over time to form the rust layer. The pollutant here is gaseous, oxygen.

### **Cathode Reaction**



### **Anodic Reaction**



### **2.0.3 Classes of Corrosion**

Corrosion can be grouped into three major categories such as:

- Chemical and Electrochemical
- High temperature and Low temperature
- Wet and Dry corrosion.

In the absence of an aqueous environment, dry corrosion typically occurs in the presence of vapors and gases, and mostly at high temperatures. When it becomes a part of an electro-chemical cell, wet corrosion is the degradation of a metal. Here you need an anode, a cathode and an electrolyte. Each type of corrosion has a particular arrangement of anodes and cathodes, and locations with specific patterns based on the type which exists. The most important examples are:

### 2.0.3.1 Fretting Corrosion

Corrosion that occurs at touch areas among substances below load subjected to slide and vibration is called Fretting. Oxidation can occur at such friction in engines and automotive parts. Fretting is understood to arise at bolted tie plates on rails. Factors that improve this particular corrosion are relative motion between the two surfaces, and interface under load.



**Fig. 2.3:** Fretting Corrosion on the inner wall of a ball bearing

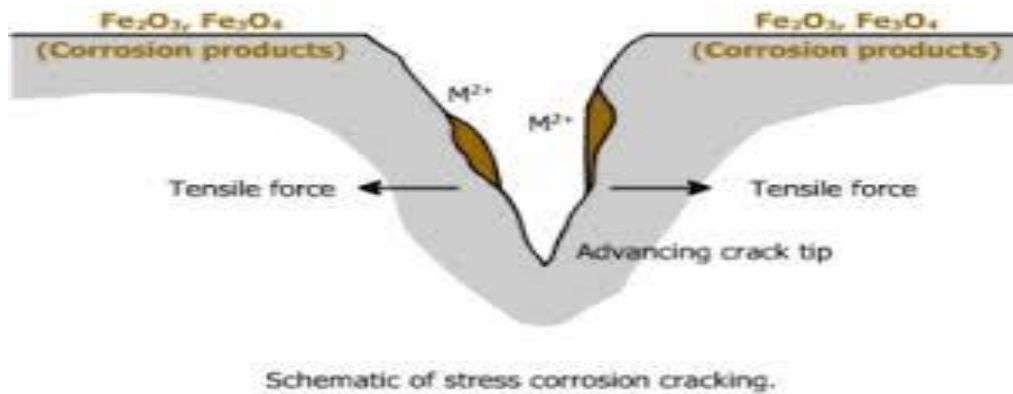
**Source:** <https://images.app.goo.gl/ZiHLq2Uv1AsyGoXT7>

### 2.0.3.2 Stress Corrosion Cracking

Stress corrosion cracking (SCC) refers to the failure under presence of a corrosive medium and tensile stress at the same time. . Caustic embrittlement of steels taking place in riveted steam-driven locomotive boilers and seasonal cracking of brass found in cases of brass cartridge due to



environmental ammonia are two classic examples of SCC. This cracking occurs differently on the type of alloys and depending on the corrosive environment. Stainless steel is seen to crack in chloride atmosphere. Major variables affecting SCC include metal/alloy composition, solution composition and structure, temperature and stress.

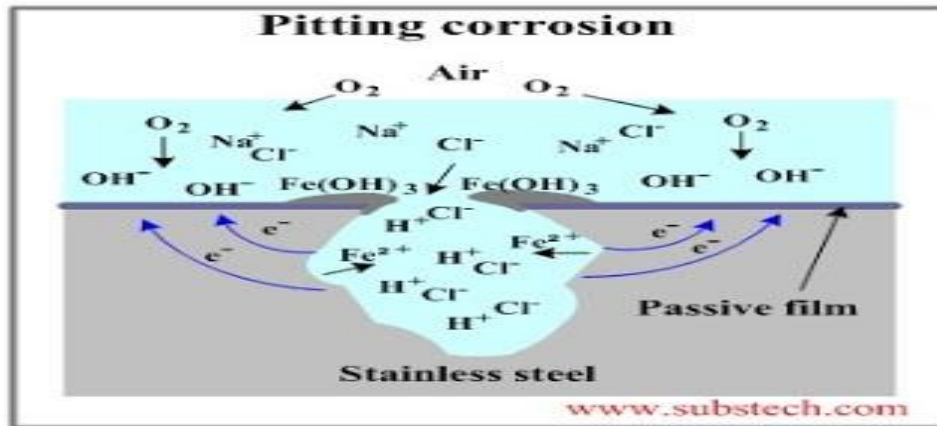


**Fig.2.4:** Stress Corrosion Cracking

**Source:** <https://www.ducorr.com/ducorr-blog/2018/5/13/causes-stress-corrosion-cracking-in-pipelines>

### 2.0.3.3 Pitting Corrosion

Pitting Corrosion Cavitations or pitting damage can be put as a unique form of erosion corrosion usually due to formation and collapse of vapor bubbles in liquids near a metal surface. Surface damages similar to pitting may occur and both corrosion and mechanical factors are involved in this corrosion. Some factors which can influence crevice corrosion include: environmental situations together with pH, temperature, oxygen concentration, halide concentrations. This is a localized phenomenon often affecting smaller areas. Formation of these micro-pits can be very damaging to the metal. Pitting factor (ratio of deepest pit to average penetration) can be used to calculate severity of pitting corrosion which is usually seen in passive metals and alloys. Tendency of pitting can be predicted through measurement of pitting potentials and temperature at which corrosion occurs is also an important parameter. This is similar to cavitations but there is a leakage on the surface of the metal to the other side.

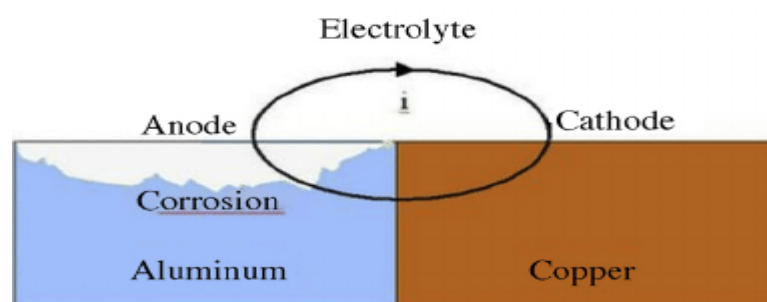


**Fig. 2.5:** Pitting Corrosion

**Source:** <https://www.hkdivedi.com/2015/11/different-forms-of-corrosion.html>

### 2.0.3.4 Galvanic Corrosion

This corrosion often referred to as dissimilar metal corrosion which occurs in galvanic couples where the active part corrodes. Different Metals and alloys have multiple potential electrodes, and when two or more come into contact with an electrolyte, one metal serves as an anode and the other as a cathode. If there is an electrolyte containing only the metal ions that are not easily reduced (such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , or  $\text{Zn}^{2+}$ ), reduction of the dissolved  $\text{H}^+$  to  $\text{H}_2$  or  $\text{O}_2$  to  $\text{OH}^-$  is the cathode reaction (Goodisman, 2001). Electro-Motive Force EMF series (thermodynamic) and galvanic series (kinetic) could be used in predicting this type of corrosion.



**Fig.2.6:** Galvanic Corrosion

**Source:** [www.researchgate.net/figure/Galvanic-corrosion-of-aluminum\\_fig1\\_288427213](http://www.researchgate.net/figure/Galvanic-corrosion-of-aluminum_fig1_288427213)

### 2.0.3.5 Uniform Corrosion

This is an abundant form of corrosion found in ferrous metals-iron containing metal and alloys that are not covered by surface coating or inhibitors. A uniform layer of rust on the surface environments is produced when exposed to corrosive material. A common example of this form is atmospheric corrosion.



**Fig.2.7:** Uniform Corrosion

**Source:** <https://www.hkdivedi.com/2015/11/different-forms-of-corrosion.html>

### 2.0.3.6 Microbial Corrosion

This is a form of bio-deterioration and is frequently referred to as bacterial corrosion, bio-corrosion, microbiologically influenced corrosion, or microbial induced corrosion (MIC). This is corrosion caused by microorganisms, usually chemo-autotrophs: organisms that manufacture their food through chemical reactions (catabolism). It applies to both metals and non-metallic materials. The only well-documented case of microbiological corrosion of aluminum is with fuel tanks of jet aircraft.

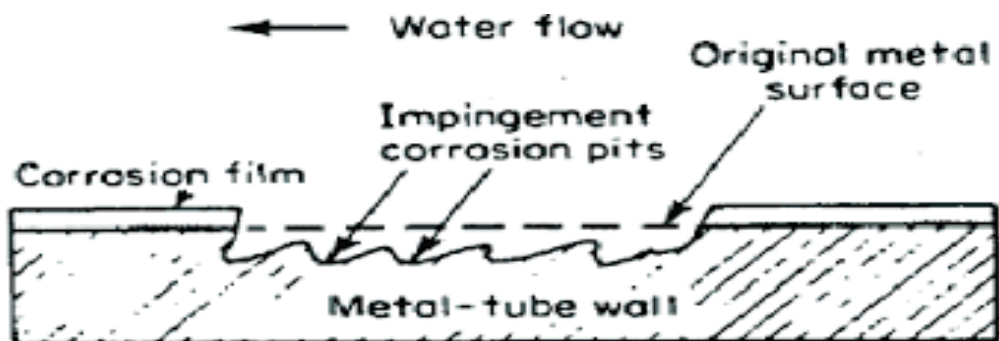


**Fig.2.8:** Microbial Corrosion

Source: BirgitH/pixelio.de

### 2.0.3.7 Erosion Corrosion

Due to relative motion between their surfaces and corrosive fluids, alloys or metals degrade. Based on the rate at which the fluid moves, abrasion happens. This corrosion form is identified by surface and grooves having direction patterns.. Stainless alloy pump impellers are common examples, and condenser tube walls. All type of equipment exposed to fluids that flows are at risk of this type of corrosion.



**Fig. 2.9:** Erosion Corrosion

Source:Pratikno and Herman (2005)

**Table 1:** Classification of types of Corrosion

<b>GENERAL CORROSION</b>	<b>LOCALIZED CORROSION</b>	<b>METALLURGY INFLENCED CORROSION</b>	<b>MECHANICAL ASSISTED CORROSION</b>	<b>ENVIRONMENTALLY INDUCED CRACKING</b>
<b>Corrosive attack dominated by uniform thinning.</b>	<b>High rate of metal penetration at specific sites.</b>	<b>Affected by alloy chemistry &amp; heat treatment.</b>	<b>Corrosion with a mechanical component.</b>	<b>Cracking produced by corrosion, in the presence of stress.</b>
Atmospheric corrosion	Crevice corrosion	Intergranular corrosion	Erosion corrosion	Stress-corrosion cracking (SCC)
Galvanic corrosion	Filiform corrosion	Dealloying corrosion	Fretting corrosion	Hydrogen damage
Stay-current corrosion	Pitting Corrosion		Capitation and water drop impingement	Liquid-metal embrittlement
General biological corrosion	Localized biological corrosion		Corrosion fatigue	Solid metal induced embrittlement
Molten salt corrosion				
Corrosion in liquid metals				
High-temperature corrosion				

(Source: Sully and Taylor, 1987)

## 2.1 CORROSION INHIBITOR

The corrosion inhibitor is one of the best known corrosion safety approaches and one of the most useful in the industry due to low costs and easy practice, among the different methods to avoid metal surface damage or degradation (Maaya et al., 2004). Any product added to an atmosphere that greatly decreases the rate of corrosion of materials is a corrosion inhibitor (especially metals). They are also substances or mixtures that when in low concentration and in aggressive environment conditions like in acidic medium; reduce the rate of corrosion (Camila et al., 2014). It is known as the first line of corrosion protection. Significant research has been carried out on government spending, mainly in broad areas, such as the production of new shale gas pipelines and construction growth.

Inhibitor in water and concrete applications for the safety of metals has been the subject of these investigations (Camila *et al.*, 2014). These inhibitors had great acceptance in the industries due to their high anti-corrosive proprieties. Many of these inhibitors caused secondary effect by damaging the environment. Thus the need for environmental friendly inhibitors gives rise to the research of organic inhibitors. Corrosion inhibitors can be grouped into two broad categories: those that increase the oxidizing effect of By selectively adsorbing the metal surface and forming a barrier that prevents corrosive agents from reaching the metal surface, the formation of a protective oxide film and others that inhibit corrosion (Buchweishaija, 2009).

### **2.1.1 Properties of a Good Corrosion Inhibitor**

A good inhibitor must possess some quality that makes it stand out with quality of good performance. Some of these are derived from the physical properties, chemical properties and the way they behave with the surface of the metal.

#### **2.1.1.1 Softness of Molecule**

A soft molecule has a small energy gap and a hard molecule has large energy gap. Hard Molecules does not act as a good inhibitor unlike soft molecules due to a large energy gap (Pearson, 1988). Soft molecule acts as better inhibitor because they interact with their electrons by donating it to the metal surface.

#### **2.1.1.2 Electro-negativity**

Higher the electro-negativity of a molecule means more bond formation or adsorption as the case my be. It affects the propensity of the molecule of the inhibitor to form complex with the metal by accepting electron(s). The inhibitor must be less electronegative than the metal, as this makes the metal attracts the electron(s) from the ligands.

### **2.1.2 Advantages of Corrosion Inhibitor**

Corrosion management can help prevent many potential disasters that can cause serious problems such as loss of life, degradation of water supplies and the atmosphere, and adverse social impacts.

Some organic compounds could be used as effective corrosion inhibitors. Organic inhibitors do not impact toxic effect on environment, aquatic and animal life and are not expensive and easy to use. They preserve the metal and in turn make it durable. They are also non-toxic and biodegradable especially from sources like plants, dyes, drugs etc.

### **2.1.3 Types of Corrosion Inhibitor**

There are different types of corrosion inhibitor. This is due to their mechanism of inhibition and mode of application.

#### **2.1.3.1 Anodic Inhibitors**

This type of corrosion inhibitor works on the surface of the metal by forming a protective oxide film. It induces a broad anode change that forces the passivation region to exist on the metallic surface, which decreases the metal's corrosion potential. Nitrate, tungstate, chromate, and molybdate are some examples.

#### **2.1.3.2 Cathode Inhibitors**

These inhibitors slow down the cathode reaction in order to limit the diffusion of reducing species to the metal surface. Oxygen scavengers and cathode poison are examples of these types of inhibitor.

#### **2.1.3.3 Volatile Corrosion Inhibitors (VCI)**

Volatile Corrosion Inhibitors (VCI) are compounds transported from a source to the corrosion site in a closed environment through the mechanism of volatilization. In boilers, for example, volatile compounds such as morpholine or hydrazine are transported by steam to avoid condenser tubes from corrosion.

#### **2.1.3.4 Mixed Inhibitors**

These are compounds that form film that decrease both the anodic and cathode reactions. Phosphates and silicates used in domestic water softeners to avoid rust water formation are the most widely used mixed inhibitors.

## 2.2. Application of Corrosion Inhibition

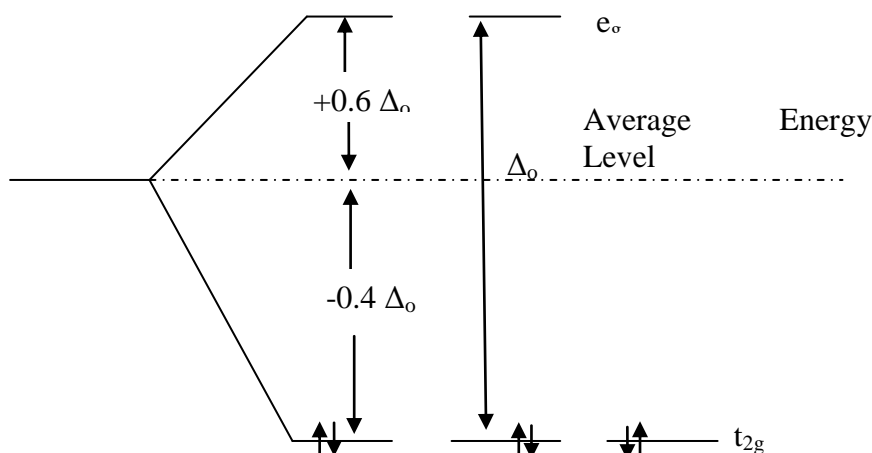
Inhibition can be applied industrially in acid pickling; where corrosion is prevented by laminating the metal (bark lamination) and to prevent hydrogen evolution, inhibitors are added examples are thioeuea and amino and derivatives (Gentil *et al.*, 2003). In oil industry, corrosion is caused by dissolution of corrosive gases. Sodium carbonates are used to reduce corrosion effect of CO<sub>2</sub>, H<sub>2</sub>S and organic acids. This makes them to be more cheap and resistant in well extraction of crude oil. In water distribution also, the most common inhibitors used are phosphates and amino volatiles (Gentil *et al.*, 2003). To also improve the durability of concretes which are affected by high alkalinity, the use of sulphate ion mixed with the cement or concrete paste practiced.

## 2.3 Mechanism of Corrosion Inhibition

Inhibitors are substances that when added into corrosive medium in small amounts, retard corrosion process. The inhibition of corrosion process is successful when  $Fe^{2+}$  is stabilized from further oxidation to  $Fe^{3+}$ . Either physisorption or chemisorption processes should readily be adsorbed to the metal surface in order for an inhibitor to be an effective protector against metal corrosion. The inhibitor group's physicochemical properties, such as the functional group, electronic density of the donor atom, molecular structure, etc., depend primarily on one of these adsorption processes. Corrosion inhibition mechanism is also accomplished in molecules possess aromatic rings, electro-active nitrogen, and oxygen atoms donating their lone pair of electrons to the metal, favoring the adsorption of these molecules on the metal surface. In addition, molecules having large and flat structure occupy a larger area of the metal surface thereby developing a protective coating. Plantain leaves on this note have inhibitive properties as they are seen physically not to get wet. They contain molecules with inhibitive properties, thereby making them worthy a study for green corrosion inhibitor. These molecules of inhibitors contain strong ligands such as  $CN$ ,  $NH_3^-$ ,  $OCN$ ,  $SCN$ , etc which causes low spin forcing the  $3d^6$  electrons into  $t_{2g}$  orbital ( $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ ). The degree of splitting is the inverse of the strength of ligands. This disrupts the degeneracy and increasing the



energy of the  $e_g$  orbital which allows for the donating of electron by the ligand to the empty  $e_g$  orbital ( $dx^2-y^2$  and  $dz^2$ ).



**Fig. 2.11:**  $Fe^{2+}$  ion and Energy levels of d orbital in octahedral field (Low

When this donated electrons by the inhibitor molecules or ions (ligand) is dative covalent bond between the metal and the inhibitor. This process produces weak bond or van der waal force of attraction which is physical adsorption (physisorption). While an ionic bonding gives rise to chemisorption due to strong electrostatic bond created. The inhibitor mechanism is usually one or more of three (3) below, and this occurs when the corrosion is blocked, prevented or reduced in a low concentration and aggressive setting. The general corrosion inhibitor function encompasses:

1. The inhibitor is chemically adsorbed (chemisorption) or physically absorbed (physisorption) on the metal surface and forms a protective thin layer of inhibitor action shapes the mixture of inhibitor ions and that of the metal on the metal surface. This film is formed by bond formation between the inhibitor ion and the metallic ions. The molecules with inhibitive properties in the plantain leaves are absorbed selectively on the surface of the metal. This results in the creation of barrier for the metal surface from corrosive agents. Chemisorption involves chemical bonds formation and breakage –absorption. It involves reaction between the metal and the components of the plant extract. While physisorption is more of a surface phenomena - adsorption. Reaction does not necessarily occur here. Any of these ways, inhibition is done.

2. The inhibitor leads to formation of the film by oxide protection on metal. Inhibition is carried out by an obstruction of the cathode reaction in addition to simulating anodic process of metal dissolution through the formation of barrier layer by blocking the reaction site (Stoyanova *et al.*, 1997). This reaction is ionic in nature. Plants generally have oxygen ( $O^{2-}$ ) stored on their leaves while the metal surface have equal but opposite charge ( $M^{2+}$ ). Extraction from these leaves is guaranteed to have oxygen related compounds which then prevent corrosion. The equal but opposite charge of the metal and the oxygen from the plantain extract bond to form a non reacting surface. In this mechanism, oxygen is the utilized only and extract not containing oxygen is considered not useful. This however, compliments the goodness of this inhibitor.
3. . The inhibitor reacts in aqueous media to a possible corrosive component and a complex is the product. Here, the plant extract's inhibitory property is not connected to the metal surface. The corrosive component and the inhibitive component react at a cancelling effect. The metal is free from corrosion as corrosive component cannot reach it as it has formed a complex (stable) with the inhibitor. Heterocyclic compounds and heteroatom containing aliphatic compounds usually participate in electron transfer adsorption via their lone pair electrons. These heteroatom and heterocyclic compounds are found naturally in plants considering plantain leaves.

## 2.4 Banana



**Fig. 2.12:** Banana tree with fruit

**Source:** <https://images.app.goo.gl/3YX66kbG2UuotggK7>

Banana is of the family of *Musaceae* with botanical name depending on the specie. Some of the specie include; *Sapientum*, *paradisiaca*, *etc.* This is a perennial fruit bearing herb plant with soft stem, having only a rhizome which serves as a true stem. It is propagated by transplanting of the stem stalk as it is sterile i.e not being able to germinate through seed. The leaves are simple with long and strong petiole that support, having an etiolate and obtuse leaf. The fruit is an elongated berry, having the edible part with the peel. A ripe fruit is seen as yellowish while unripe is greenish. Banana serves different purposes like for food, medicine, horticulture, pharmacology; antiseptic, antiepileptic amongst other pharmaceutical activities.



**Fig. 2.13:** Banana fruit

**Source:** <https://images.app.goo.gl/pqUYk1aiYnV68i2S8>

## **CHAPTER THREE**

### **3.0 Materials**

The materials used includes MPL extracts, organic solvents (ethanol), separating bottle, Erlenmeyer flask, Buchner funnel, suction pump, filter papers, oven, reflux system, sample bottles, beakers, rotary evaporator, retort stand, glass funnel, distilled water, reagents,

### **3.1 Methods**

#### **3.1.1 Extraction of Inhibitors**

##### **3.1.1.1 Preparation of Plant**

Fresh leaves of banana were gathered in large quantity, selected from around same source, to ensure no contaminated leaves of different plant or specie. The leaves were cleaned and dusted and finally washed with running tap water to remove impurities. The leaves were air-dried at room temperature, shredded into smaller pieces to reduce leaves surface area, thereby increasing drying. This is done until the leaves are no greener indicating they were dried, for about 3 weeks. In order to remove moisture content from the leaves and to aid pulverization, the dried leaves were oven-dried at 90 °C for about 2 hours until the sample were crispy. The crisp sample from the oven was immediately pulverized. It was then crushed (to reduce the size) and then pulverized using an industrial blender while still crispy. The powdered leaves (sample) were then stored in an air-tight glass bottled and covered.

##### **3.1.1.2 Extraction Process**

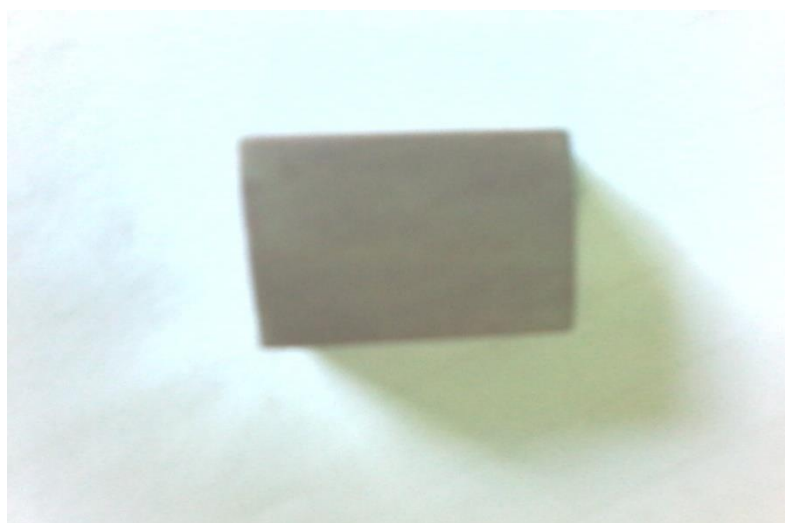
Using 70% ethanol for solvent extraction at room temperature, the pulverized sample of MPL was soaked for 48 hours until a dark-green color was observed indicating that extraction has taken place. The darkish-green solution was filtered out which contains the plant extract while the residue is the chaff from pulverized leaves. The procedure was repeated on the chaff to ensure maximum extraction.

### 3.1.1.3 Purification and Concentration

Purification involved separation and refluxing for specific period of time. After separation of the filtrate using a separation funnel, the organic layer is the desired sample was then refluxed to ensure homogeneity of the sample. Here, bonds were broken and made within the molecules of the sample. The product of purification was then concentrated in order to be stored for further usage. The concentration of the extract of plants was carried out using a Rotary Evaporator which removes solvents from the extract thereby making it slurry.

### 3.1.2 Preparation of Metal Coupons

The specimen of mild steel was machined into rectangular coupons by lathe machine of dimension 20.21 mm by 14.63 mm as shown in Fig. 3 below. The edge of the coupons was polished with emery paper of 600 grades. The thickness was determined with Mitutoyo brand of analog micrometer screw gauge while the dimension by Mitutoyo digital vernier gauge of 2 decimal places. The surface treatment of the coupons were without further polishing but grease on their surfaces were removed by immersion in absolute ethanol and then rinsed with double distilled water and acetone. They were then stored in moisture free desiccators to prevent rusting or contamination before use (Shittuet *al.*, 2004)



**Fig. 3.1** Metal coupons for corrosion test

## **3.2 Method of Characterization**

### **3.2.1 GC-MS**

This analysis was performed using 7820A gas chromatograph coupled to 5975C inert mass spectrometer (with triple axis detector) and electron impact source (Agilent Technologies). The stationary phase of separation of the compounds was carried out on HP-5 capillary column coated with 5% of Phenyl Methyl Siloxane (30 m length  $\times$  0.32 mm diameter  $\times$  0.25  $\mu$ m film thickness) (Agilent Technologies). Helium was used in the carrier gas at a steady flow rate of 1,573 ml/min, an initial nominal pressure of 1,9514 psi and a mean velocity of 46 cm/s. One micro liter of the samples was injected at an injection temperature of 260 °C in split less mode. With a total gas flow rate of 23.355ml/min, the purge flow was 21.5 ml/min at 0.50 min; the gas saver mode was turned on. The oven was initially programmed at 60 °C (1 min), then ramped to 110 °C (3 min) at 4 °C / min, accompanied by program temperature speeds. Initially, the oven was programmed at 60 °C (1 min), then ramped up to 110 °C (3 min) at 4 °C / min, followed by program temperature thresholds of 8 °C / min to 260 °C (5 min) and 10 °C / min to 300 °C (12 min). The run time with a solvent delay of 3 min was 56.25 min. The mass spectrometer was run at 70eV with 230 °C ion source temperature, 150 °C quadruple temperature, and 280 °C transfer line temperature in electron impact ionization mode. Scanning of potential compounds was at 2.62s/scan rate from m/z 30 to 550 amu and was recognized by comparing measured mass spectral data with those in the NIST 14 Mass Spectral Library (Altameme, 2015)

### **3.2.2 FT-IR**

FT-IR Spectroscopy is a proven quality management technique when evaluating material synthesization. It is the first step in the analysis process of material. It is useful for analyzing chemical components of smaller particles typically 10-15microns. Using infrared as source of energy to scan test samples and observe chemical properties. The FT-IR instrument introduces infrared radiation of about 10,000 to 100 cm<sup>-1</sup> through the sample. Some radiation is absorbed while some are transmitted.

The radiation that is absorbed is converted into vibration and/or rotational energy by the molecules of the sample. The resulting radiation transmitted from the sample is the molecular finger print of the sample. The signal at the detector presents a spectrum typically from 4000cm<sup>-1</sup> to 400cm<sup>-1</sup>. Each molecule produce a different fingerprint. Fourier Transform Infrared (FT-IR) spectroscopy investigations of the various functional groups present in the HAp powder were carried out using TENSOR 27 series FT-IF spectrometer, Germany. The KBr pellet technique was used in which 1.99% of the synthesized HAp powder and KBr is combined in a mortar and pestle and then compressed to a 2 mm diameter pellet ratio. All FT-IR spectra data were recorded in the range of 4000cm<sup>-1</sup> to 400cm<sup>-1</sup> with resolution of 4cm<sup>-1</sup> and 64 times scanning.

### **3.3 Weight Loss Determination of Extract Inhibition**

Mild steel of 20.21 mm by 14.63 mm were used for weight loss measurement. The total geometric surface area of the coupons exposed to the corroding agent was about 295.67 mm<sup>2</sup> and average weight of coupons was 13.18 to 15.61 grams. The weighed coupons were immersed in 20 mL sample bottles containing concentration of corroding agent, HCl to that of the extract (*Musa paradisiaca*) as: 20:0 v/v, 15:5 v/v, 10:10 v/v, 5:15v/v at 25 ± 2 °C and 60 °C consecutively for 72 hrs. This procedure is repeated further for 1M and 2M of HCl at 60°C. The weight loss experiment is used to calculate the inhibition efficiency, corrosion rate and also the half-life of the metal coupon.

## CHAPTER FOUR

### 4.0 RESULTS AND DISCUSSIONS

#### 4.1 CHARACTERIZATION

##### 4.1.1 Elementary Analysis of the Mild Steel

**Table 4.1:** Elementary Composition of Mild Steel

ELEMENTS	%COMPOSITION	ELEMENTS	%COMPOSITION
Fe	98.88	Mo	0.0474
C	0.1115	Cu	0.0573
Si	0.0420	Al	0.0202
Mn	0.3375	V	0.0084
P	0.261	Co	0.0299
S	0.0347	Nb	0.0548
Cr	0.0448		
Ni	0.2051		

From **Table 4.1** above, the elemental analysis of the mild steel showed the following elemental composition: *Fe* (98.88%), *c* (0.1115%), *Si*(0.0420%), *Mn* (0.3375%), *P* (0.261%), *S* (0.0347%), *Cr* (0.0448%), *Ni* (0.2051%), *Mo*(0.0474%), *Cu* (0.0573%), *Al* (0.0202%),*V* (0.0084%) and *Nb* (0.0548%). It was observed that *Fe* has the largest proportion in the metal matrix of the Mild Steel and *V* had the lowest proportion.

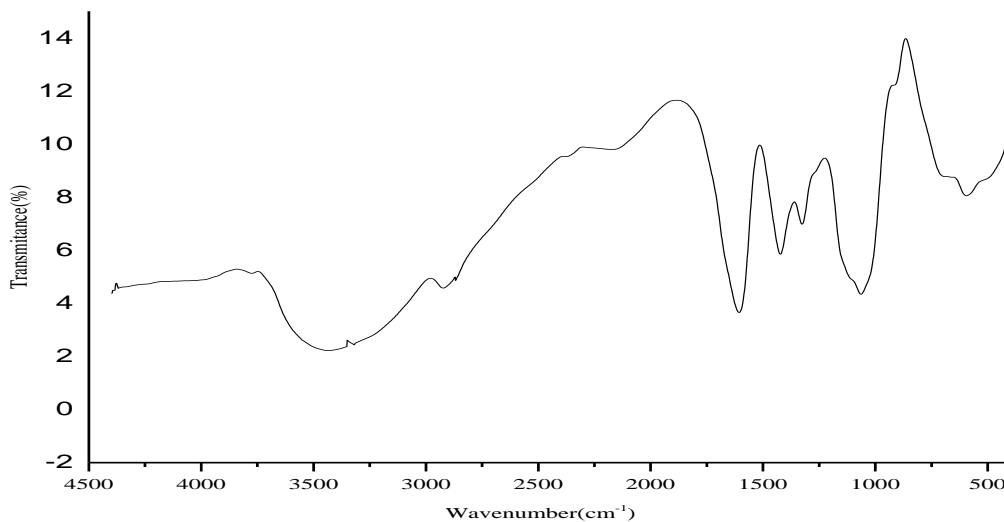
##### 4.1.2 FT-IR Analysis

FT-IR was used to identify the functional groups present in the extract. The FT-IR spectra as shown in Fig. 2 below, while the assignments of the various functional groups present are indicated in Table 4.2

In the FT-IR spectra, the absorption bands belonging to the O-H and N-H stretching vibrations were observed between 3325 – 3567  $\text{cm}^{-1}$ , while the C-H stretching vibrations was noted between 2378 – 2987  $\text{cm}^{-1}$ . The vibration of C=C bond was observed at the around 1645  $\text{cm}^{-1}$ , while that corresponding to C-N vibration stretching was observed at 1248  $\text{cm}^{-1}$ . The absorption bands which occurred between 1098 and 1102  $\text{cm}^{-1}$  were assigned to C-O functional group. FT-IR of the extract



showed the presence of oxygen and nitrogen atoms in functional groups. The presence of oxygen and nitrogen atoms in the extracts met the general characteristics of a typical corrosion inhibitor.



**Fig. 4.1:** FT-IR Analysis of *Musa Paradisiacal* Leaves

**Table 4.2:** FT-IR Spectra of *Musa Paradisiacal* Leaves

Wave number (cm <sup>-1</sup> )	Vibration mode
3325 – 3567	O-H and N-H stretching
2987	C-H stretching
2378	C-H stretching
1645	C=C stretching
1462	Methyl C-H stretching
1248	C-N stretching
1098 – 1102	C-O stretching

### 4.1.3 Extractive Content Using GC-MS

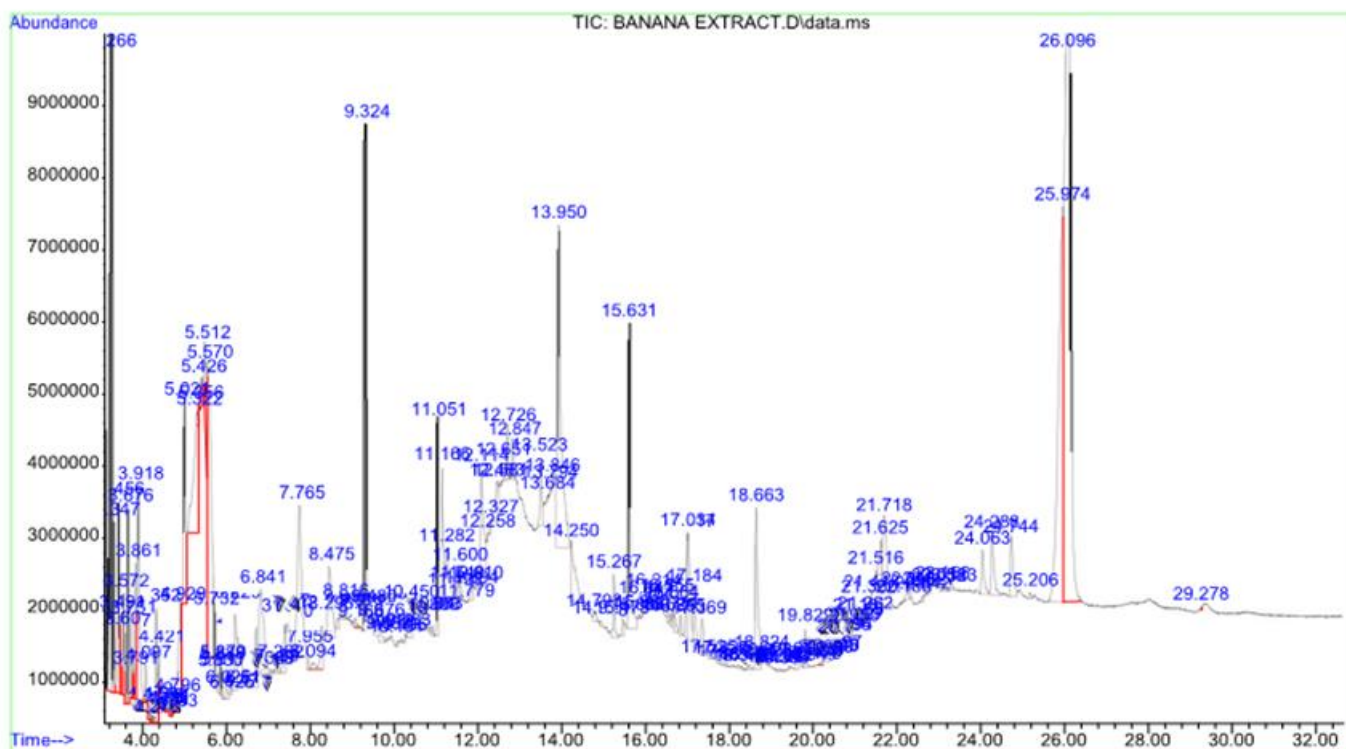


Fig. 4.2:GC-MS Chromatogram of MPL extract

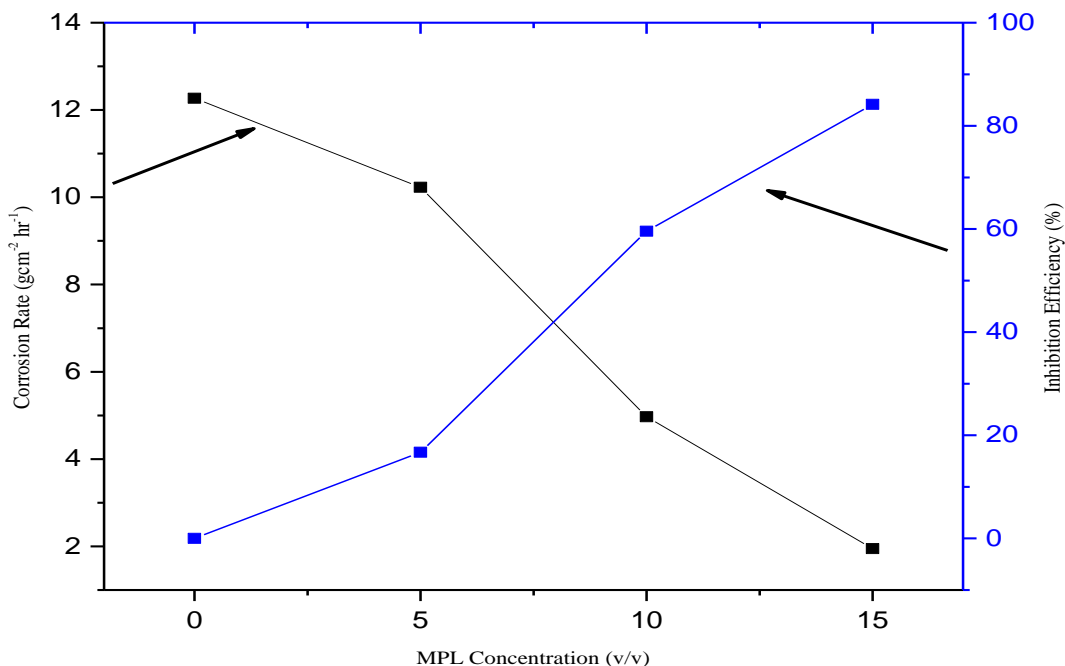
Table 4.3: MPL extract characterization using GC-MS

Retention time	Compound Name	Molecular formula	Molecular Weight (g.mol <sup>-1</sup> )	Estimated Conc.
6.841	6-Amino-1,3,5-triazine-2,4(1H,3H)-dione	C <sub>3</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>	128.09	27
6.841	9-Octadecenamide, (Z)- <b>OLEAMIDE</b>	C <sub>18</sub> H <sub>35</sub> NO	281.477	98
12.726	Polygalitol	C <sub>6</sub> H <sub>12</sub> O <sub>5</sub>	164.16	49
9.324	Cyclotetrasiloxane, octamethyl-	C <sub>8</sub> H <sub>24</sub> O <sub>4</sub> Si <sub>4</sub>	296.6152	87
8.475	Thiophene, 2,3-dihydro-	C <sub>4</sub> H <sub>6</sub> S	86.16	50
24.063	Ginsenosol	C <sub>15</sub> H <sub>26</sub> O	222.3663	38

For the inhibition process, the presence of polar functions with S, O or N and p-electrons of the plant extract is typically considered to be the center point. Gas chromatography–mass spectrometry (GC–MS) analysis of plant extracts revealed different biomolecules and suggesting that the plant extract consists of different molecules as listed in Table 4.2 with the microgram shown in Figure 4.2. It should be noted that O, N or S and/or p-electrons are present in almost all the identified biomolecules from the plant extracts. Plant extracts are known to consist of different mixture of organic compounds containing O, S, N or p-electrons in their structures. Thus, the corrosion inhibition of mild steel by MPL extract can be assigned to the presence of these phytochemicals which are made up of S,N, O, and other hetero atoms in their structures which are responsible for donating electrons to inhibit the corrosion process and thus serving as centers of adsorption onto the metal surface.

#### **4.1 Effect of *Musa Paradisiaca* Leaves (MPL) Concentration**

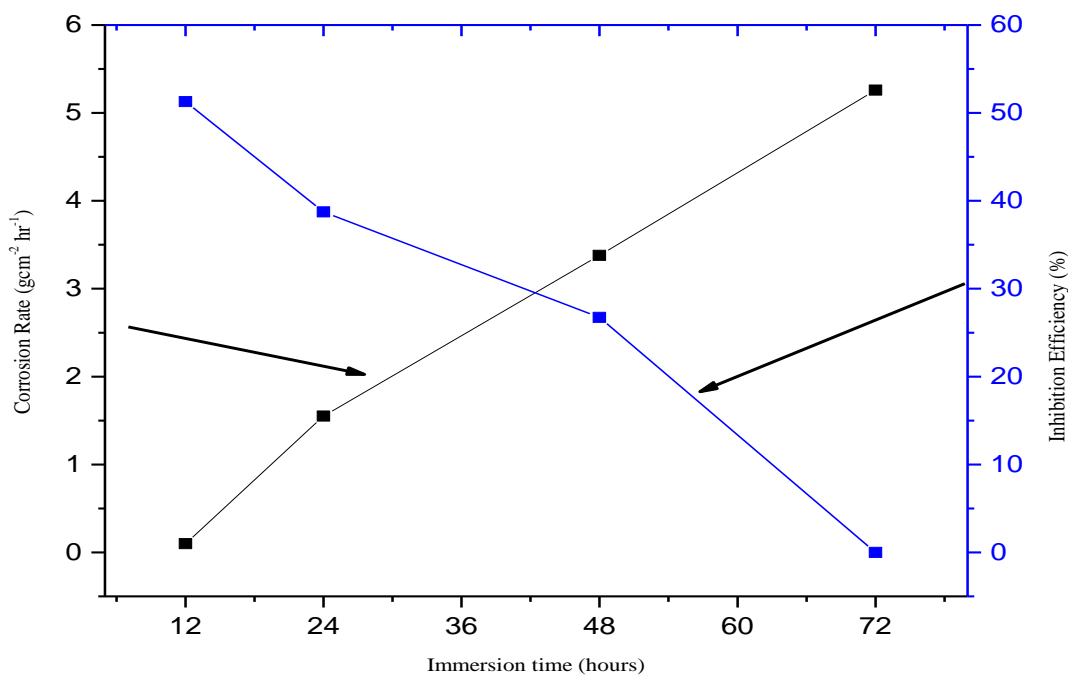
The calculated inhibition efficiencies (IE) and corrosion rates (CR) of *M. paradisiaca* (MP) in curbing corrosion in mild steel immersed in HCl are shown in Figure 4.3. The calculated values indicate the ability of MPL to be a good corrosion inhibitor. The inhibitory efficiency I.E. is found to be increasing with the concentrations of *M. paradisiaca* leave extract, while the corrosion rate was seen decreasing. Maximum inhibition efficiency was attained at a concentration of 5-15% v/v of *M. paradisiaca* leaves extract. As seen in the Fig 4.2 below, change in the concentration of the inhibitor at constant temperature yields a decline in weight loss and corrosion rate, and an increase in inhibition efficiency and surface coverage.



**Fig4.3:**Effect of *Musa paradisiaca* concentration on the Inhibition Efficiency and Corrosion Rate

#### 4.2 Effect of Immersion Time

The variation of inhibition performance of *Musa paradisiacal* leave extract as well as the corrosion rate with immersion time at concentration of 5-15% v/v is shown Figure 4.4. The weight loss study results indicated the increase in corrosion rate with increase in time of immersion till 72 h. The best performance of the MPL has been perceived at 12 h of immersion period with the entire concentration of the inhibitor. Marginal inhibition sets in after the 48 hours due to the less effectiveness of the inhibitor due to over long reaction with the acid. Desorption occurs with prolonged exposure of the inhibitor to the acid medium. Although, I.E. was noticed to have decreased with increased immersion time, but this phenomenon could be blamed on desorption of the plant extract which initially prevent corrosion from taking place and also, at initial stage of the immersion, the inhibitory efficiency of the active components of the plant are high but as the reaction proceed, these active components are used up, thus given rise to increase in corrosion rate. More also, the presence the corroding agent over long time the corrosion will become abundant.

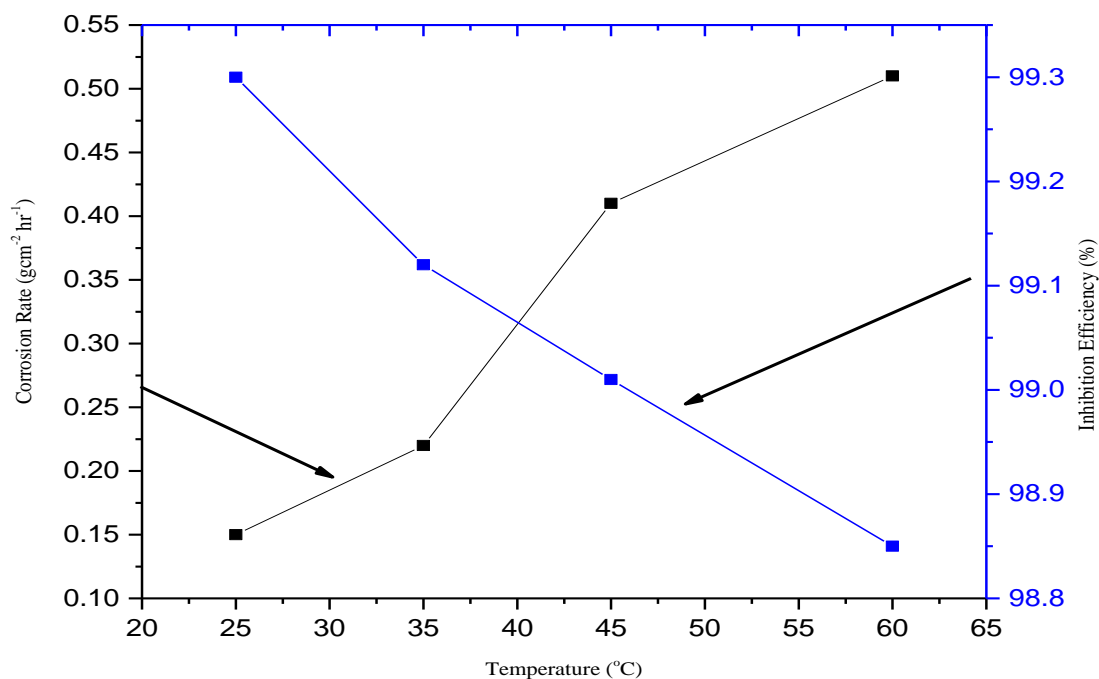


**Figure 4.4:** Effect of immersion time on the corrosion rate and inhibition efficiency of *Musa Paradisiaca*

### 4.3 Effect of temperature

Changes occur on the metal surface such as desorption of inhibitor or decomposition of the inhibitor (Bentisset *al.*, 2005). The change in corrosion rate (CR) at selected concentration of MPL extract during 12hrs of immersion at two temperatures ( $25\pm 2$  and  $60^{\circ}\text{C}$ ) was studied in 1M HCl, while putting into constant immersion time and concentration as indicated in Figure 4.5. It was observed that inhibitor efficiency (IE) decreased with an increase in temperature. The drop in temperature IE may be due to the desorption at higher temperatures of the inhibitor molecule from the metal surface (Shukla and Quraishi, 2010). Corrosion rate (CR) increased as temperature increased due to the desorption of the bio-molecules of MPL extract from the metal surface, resulting in more area of the metal surface being exposed to acidic medium. An increase in temperature also brings about increase in weight loss and increase in corrosion rate, CR (Shukla and Ebenso, 2011). When the inhibitor covers the surface of the metal, it is hard for corrosion to take place since the surface of the metal has been coated. It takes

time for the inhibition coating to wear off and consequently, this slows down corrosion (Shukla and Ebenso, 2011). But when temperature increases, it causes the inhibitor to fall from the surface of the metal thereby, causing an increase in corrosion rate, and decrease in inhibitory efficiency. The drop in the physisorption at higher temperature agrees that inhibition on the metal surface is physical in nature.



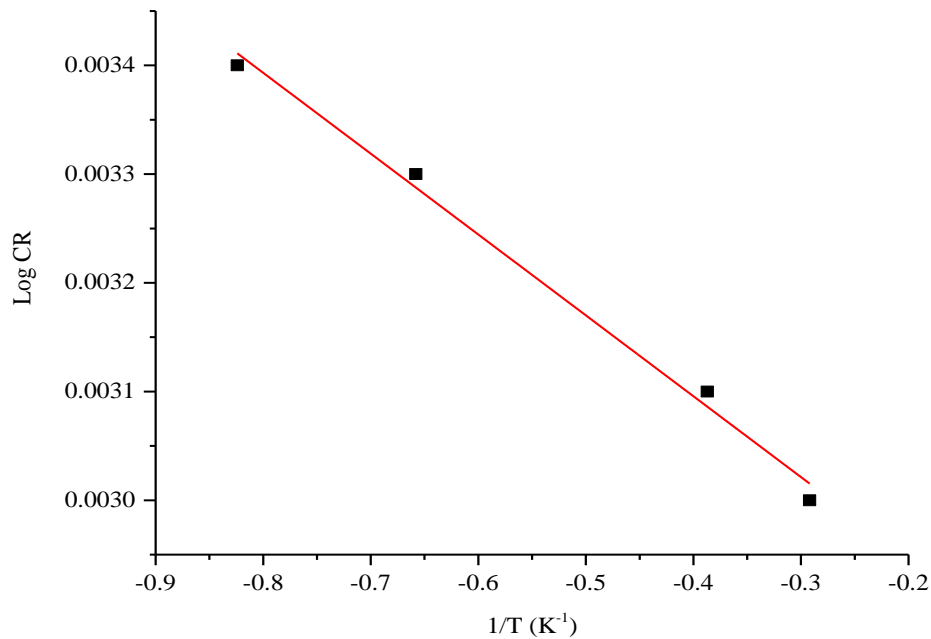
**Fig. 4.5:** Effect of Temperature

#### 4.4: Thermodynamic Study

Thermodynamic properties such as activation energy ( $E_a$ ), free energy change ( $\Delta G$ ), entropy change ( $\Delta S$ ) and enthalpy change ( $\Delta H$ ) were estimated to further examine the impact of temperature on the inhibitory efficiency of the inhibitor. All chemical reactions need a minimum amount of energy for the reaction to proceed. This energy is known as activation energy. Low activation energy implies that the reaction is likely to occur spontaneously or without the intervention of catalyst and this was calculated using Arrhenius equation below:

$$\text{Log CR} = \text{Log A} - \frac{E_a}{2.303R} \left(\frac{1}{T}\right) \quad (1)$$

Where CR is the corrosion rate,  $E_a$  is the activation energy, R is the molar gas constant and T is the temperature. Then, the slope of the graph of log CR versus  $1/T$  as shown in Figure 4.6 was used to calculate the activation energy as presented in Table 4.3. The value of the activation energy determined is 0.014kJ/mol/K.



**Fig.4.6:** A plot to determine Activation Energy

The enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) were estimated from the slope and intercept of equation 2. The plots of  $\ln\left(\frac{CR}{T}\right)$  against  $\frac{1}{T}$  is shown in Figure 4.7, while their physical values are as presented in Table 4.3.

$$\ln\left(\frac{CR}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^\theta}{R} - \left(\frac{\Delta H^\theta}{RT}\right) \quad (2)$$

Where h –Planck's constant, N –Avogadro's number, R –gas constant, T –temperature and CR is corrosion rate.

The free energy change is concerned with how feasible and spontaneously a reaction will occur and this was obtained using equation 3 below:

$$\Delta G = -RT \ln(55.5K) \quad (3)$$

and  $K$  is given as:

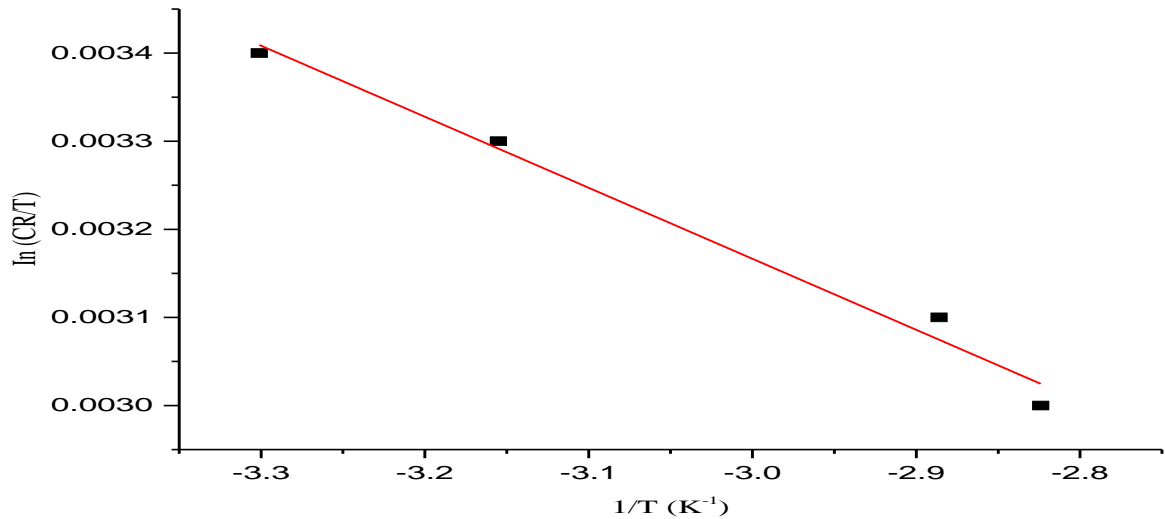
$$K = \frac{\theta}{C(1-\theta)} \quad (4)$$

Where  $\theta$  degree of coverage on the metal surface,  $K$  is equilibrium constant,  $R$  is a constant,  $C$  is the concentration of the inhibitor, and  $T$  is temperature. A negative value of  $\Delta G$  was obtained, showing that it is a spontaneous reaction. This is also used to determine the pathway of the experiment – physisorption or chemisorptions. At a value of up to  $-20 \text{kJmol}^{-1}\text{K}^{-1}$  is physisorption, whilst the value of  $\Delta G$  up to  $-40 \text{kJmol}^{-1}\text{K}^{-1}$  and higher is said to be chemisorption. From this present study, the value of  $\Delta G$  obtained from the study of MPL extract inhibit on mild steel in HCl ranges between  $-5.56650$  and  $-4.95783 \text{kJmol}^{-1}$  which further indicate that the reaction pathway of corrosion on mild steel in HCl is a typical physisorption at the studied temperatures.

Enthalpy, on the other hand is seen to be positive, depicting an endothermic reaction. Corrosion is known to be a exothermic reaction, because it increases with increase in temperature and this temperature comes from the surrounding. The value of enthalpy obtained from this study is  $6.72 \text{kJ/mol/K}$ . This indicates that the process of inhibition of the surface of the metal by the inhibitor (MPL) is endothermic in nature. It has been noted from experiment that high enthalpy (+) value and low entropy (-) is best for inhibition which is in line with what was observed in this study. Entropy depicts the degree of disorderliness of a slope and this is brought about by high temperature that causes the molecule to move randomly due to gained energy. From the experimental result, it was



gathered that with low entropy, inhibition efficiency is at maximum. This agrees with the fact that increase in temperature reduces inhibition and increase in corrosion rate (Shukla and Ebenso, 2011).



**Fig 4.7:** A plot to determine entropy and enthalpy

**Table 2:** Thermodynamic properties of inhibition of MPL on metal surface

Temperature (K)	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (kJ/mol)	E a (kJ/mol)
298	-5566.50	6.72	-197.53	0.014
308	-5104.37			
318	-4989.13			
333	-4957.83			

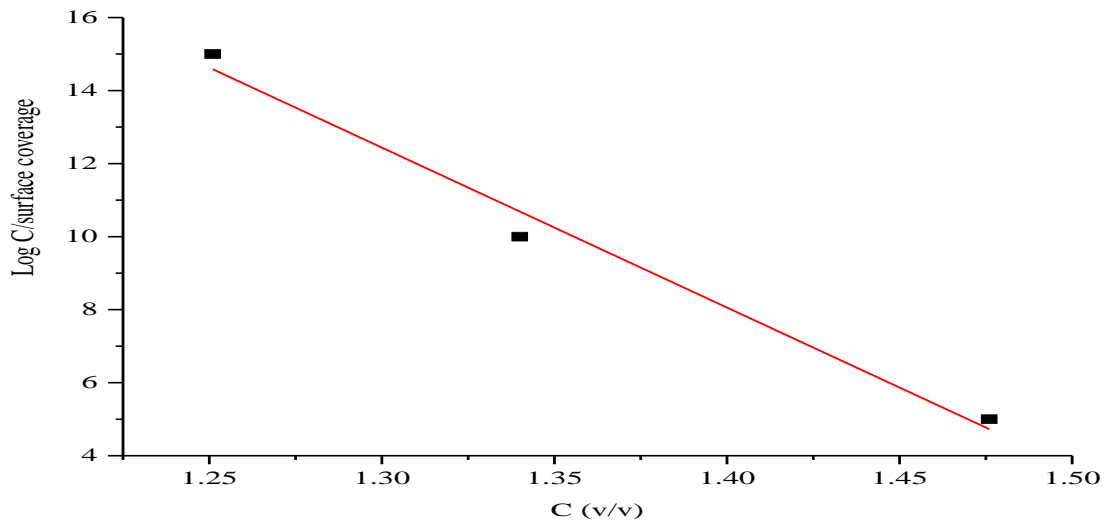
#### 4.5: Isotherms Study

Adsorption isotherm can reveal information relating to the adsorption mechanism, surface coverage, and adsorption equilibrium constant. To verify the isotherm, the linear relation that exists

between the surface coverage degree ( $\theta$ ) and inhibitor concentration ( $C$ ) was established using the value of the correlation coefficients ( $R^2$ ) as illustrated in Figure 5.

$$\log \frac{C}{\theta} = \log C - \log b \quad (5)$$

Where,  $C$  is concentration of the inhibitor,  $\theta$  is surface coverage degree of the inhibitor on the metal surface and  $b$  is the inhibitor adsorption process equilibrium constant. Figure 4.8 shows the plots of  $\log C/\theta$  against the inhibitor concentrations ( $C$ ) at 303K. From the calculated value of correlation coefficients ( $R^2$ ) which is 0.971, it can be said that the Langmuir isotherm can also be use to describe the inhibition process which assumed a physical reaction with weak intermolecular forces.



**Fig 4.8:** Isotherm plot of Langmuir isotherm

## **CONCLUSION**

The extraction of the inhibitor at 48 hours using 70% ethanol from MPL was reported. The Extract was characterized by FT-IR and GC-MS methods. The results of inhibition efficiency and corrosion rate were calculated using weight loss method. It was also established that corrosion rate is inversely proportional to the Inhibitory Efficiency (I.E.) and directly proportional to half-life. When considered, the plant extract was noticed to have reduced corrosion. As studied shows, all the above results are in line with the core purpose of this research which is to prove the inhibitive property of Banana leaves. This in turn proved the essence of the study in similarity with the idea of other researchers as referenced. This show that the plant inhibitor extracted is efficient, serving its purpose by minimizing weight loss of the metal.

## **RECOMMENDATION**

There should be more research effort in making use of plants as inhibitors for applications in industries. This approach is more environmental friendly compared of the toxic caused by inorganic inhibitors. Government should also make available grants for the effective study of this area of chemistry which has been proven to be renewable and environmental friendly.

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## APPENDIX I

### For weight loss

$$\Delta W = (W_i - W_f)g \quad (1)$$

Where:

$\Delta W$  = weight loss of coupon,

$W_i$  = Initial weight of coupon

$W_f$  = Final weight of coupon

### For Corrosion Rate

$$CR, \rho (mg \text{ cm}^{-2} \text{ h}^{-1}) = \frac{\text{Weight}_{-}\text{Loss}(mg)}{\text{Surface}_{-}\text{Area}, S(\text{cm}^2) \times \text{Time}, t(\text{hr})} \quad (\text{Ishtiaque } et \text{ al.}, 2010) \quad (2)$$
$$= \frac{\Delta W}{St}$$

Where

CR =  $\rho$  = Corrosion rate  $\text{gcm}^{-2} \text{ min}^{-1}$  or  $\text{gcm}^{-2} \text{ hr}^{-1}$

$\Delta W$  = weight loss

S = Surface area

t = immersion period

The inhibition efficiency can be obtained by using equation 3a or 3b below

$$I.E. \% = \left[ \frac{W_u - W_i}{W_u} \right] \times 100 \quad (3a)$$

$$I.E. \% = \left[ \frac{\rho_1 - \rho_2}{\rho_1} \right] \times 100 \quad (3b)$$

Where:

I.E. = Inhibition Efficiency

$W_u$  = Weight of uninhibited

$W_i$  = Weight of inhibited

$P_1$  = Corrosion rate of uninhibited

$P_2$  = Corrosion rate of inhibited

### For calculating Percentage extract yield

$$\% \text{ Extraction Yield} = \frac{W_1 - W_2}{W_1} \times 100 \quad (4)$$

Where

W1 is weight of extract before extraction

W2 is weight of extract after extraction

**Surface coverage determination for Isotherm calculations**

$$\theta = \frac{I.E}{100} \quad (5a)$$

Where

$\theta$  = Surface Coverage

I.E. = Inhibition Efficiency

## APENDIX II

**Table 5.1:** Effect of the Concentration of *Musa paradisiaca* Leaves (MPL) Extract

MPL Concentration (v/v)	Corrosion Rate (CR) $\text{mg}\cdot\text{mm}^{-2}\cdot\text{s}^{-1}$	Inhibition Efficiency (IE) (%)	Half-life (mm/yr)
20-0%	12.27	0	15.77
15-5%	10.23	16.7	13.17
10-10%	4.97	59.56	6.365
5-15%	1.95	84.17	2.465

**Table 5.2:** Effect of Immersion Time

Contact time (hour)	Corrosion Rate (CR) $(\text{mg}\cdot\text{mm}^{-2}\cdot\text{s}^{-1})$	Inhibition Efficiency (IE) (%)	Half-life (mm/s)
12	0.1	51.29	0.082
24	1.55	38.73	0.087
48	3.38	26.74	0.067
72	5.26	0	0.237



**Table 5.3:**Effect of Temperature

Temperature (°C)	Corrosion Rate (CR)(mgcm <sup>-2</sup> s <sup>-1</sup> )	Log CR	Inhibition Efficiencies (IE) (%)	Half life	CR/T	Log CR/T	1/T
25 ± 2=298	0.15	-0.824	99.30	0.082	0.0005	-3.301	0.0034
35=308	0.22	-0.658	99.12	0.117	0.0007	-3.155	0.0033
45=318	0.41	-0.387	99.01	0.128	0.0013	-2.886	0.0031
60=333	0.51	-0.292	98.85	0.136	0.0015	-2.824	0.0030

**Table5.4:** Values for calculating Gibbs free energy

Temperature (°C)	Inhibition Efficiencies (IE) (%)	1/T (s <sup>-1</sup> )	$\theta = \frac{IE}{100}$	C(1- $\theta$ )	$K = \frac{\theta}{C(1- \theta)}$	$\Delta G = -RT \ln K$
25 ± 2=298	99.30	0.0034	0.993	0.105	9.457	-5.56650
35=308	99.12	0.0033	0.991	0.135	7.340	-5.10437
45=318	99.01	0.0031	0.99	0.15	6.600	-4.98913
60=333	98.85	0.0030	0.989	0.165	5.994	-4.95783

R = 8.314 Kj/mol/K