

**ANTICORROSION PERFORMANCE OF  
CHRYSOPHYLLUM ALBIDUM AND A SYNTHETIC  
INHIBITOR IN SIMULATED DRILLING FLUID**

**BY**

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**20124763538**

**A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL  
FEDERAL UNIVERSITY OF TECHNOLOGY, OWERRI,  
IMO STATE**

**SEPTEMBER, 2019.**

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


**SEPTEMBER, 2019.**

## CERTIFICATION


This is to certify that this work Titled "Anti-Corrosion performance of Chrysophyllum Albidum and a Synthetic Inhibitor in Simulated Drilling Fluid" was carried out by ACHINIHU IKECHUKWU OBINNA with (Reg No. 20124763538) in partial fulfillment for the award of the degree of M.Sc. in Physical Chemistry in Department of Chemistry, Federal University of Technology Owerri.

  
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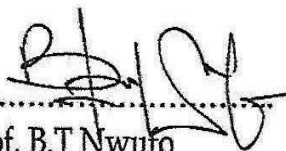
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## **DEDICATION**

This work is dedicated to the Almighty God.

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May I use this medium to appreciate enormously the efforts of my amiable supervisor Professor Emeka .E Oguzie, for his guidance and contributionstowards this work. I pray the Almighty God in His infinite grace to continue to strengthen him.In addition, I acknowledge the effortsof my co – supervisor, Dr. C. O. Akalezi for his encouragement.

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## LIST OF ABBREVIATIONS

1.	C. A	Chrysophyllum Albidum
2.	S.I	Synthetic Inhibitor
3.	W.L	Weight Loss
4.	I.E	Inhibition Efficiency
5.	C.R	Corrosion Rate

## ABSTRACT

The anti-corrosive performance of ethanol extracts of *Chrysophyllum albidum* and a synthetic inhibitor was investigated using weight loss and potentiodynamic polarization technique on mild steel. Results from weight loss analysis revealed that inhibition efficiency increased with increase in concentration of the inhibitors while corrosion rate decreased with increase in concentration of the inhibitors due to the adsorption of the organic molecules on the metal surface. Highest inhibition efficiency of 96.6% at 218.2 ml/L was recorded after five days for the ethanol extracts of *Chrysophyllum albidum* and 96.05% at 250ml/L after three days for the synthetic inhibitor both in a simulated drilling fluid. Temperature studies carried out also revealed the efficacy of the ethanol extracts of *Chrysophyllum albidum* compared to the synthetic inhibitor at the temperature ranges of 313K and 333 K. From the values of activation energy obtained, the mechanism of the adsorption process was proposed to be predominantly of chemisorption for both inhibitors. The values of  $\Delta G$  obtained were all negative which reveals spontaneity of the process while  $\Delta H_{ads}$  reveals endothermic reactions for both inhibitors in the simulated drilling fluid medium. Potentiodynamic polarization results showed that both the anodic and cathodic reactions were inhibited indicating that the inhibitors are of mixed type. The experimental data obtained fits well with Langmuir adsorption isotherm indicating that the inhibitors were adsorbed uniformly on the metal surface.

**Key Words:** Chrysophyllum Albidum, Corrosion Inhibition, Weight Loss, Mild Steel, Synthetic Inhibitor.

## CHAPTER ONE

### INTRODUCTION

#### 1.1 BACKGROUND INFORMATION

##### 1.1.1 PREAMBLE

The uses of mild steel cut across several sectors. These include petrochemical, food, sugar, leather, textile industries etc. Corrosion of metals is a common problem that has economic as well as environmental impact. Many of the corrosion problems encountered in our industries are engendered by acids such as HCl, H<sub>2</sub>SO<sub>4</sub>, and to a reduced extent H<sub>2</sub>CO<sub>3</sub>, (Sastri, 1998). In the oil industries, corrosion in various forms is the major cause of drilling pipe failures that add significantly to drilling costs (Kermani&Morshed, 2003). The trends toward drilling of deeper wells, use of higher strength steels, presence of higher stresses, and use of lower pH drilling fluids contribute to increased susceptibility of metals to failure because of corrosion (Anom, 2006).

Corrosion is the principal cause of damage to metals in wells and production facilities. Corrosion attacks metals in drilling and producing operations through electrochemical processes in the presence of electrolytes and corrosive agents in drilling, completion, packer, and produced fluids. The components in fluids that promote the corrosion of steel in drilling and producing operations are majorly oxygen, carbon dioxide, hydrogen sulphide (Chilingarian, Mourhatch, & Al-Qahtani, 2008).

Because it is almost impossible to prevent corrosion, it is becoming more apparent that controlling the corrosion rate may be the most economical solution. Corrosion engineers

are therefore increasingly involved in estimating the cost of their solutions to corrosion prevention and estimating the useful life of equipment (Singh & Krishnathan, 2009).

Recent researches in the field of corrosion have been geared towards reduction if not complete eradication through the use of synthetic and inorganic inhibitors. This is simply so owing to the health and environmental hazards posed by this class of inhibitors. Apart from being hazardous, synthetic inhibitors are expensive, not readily available, non – biodegradable, non-renewable and more especially, are not eco- friendly (Oguzie, Onuoha, & Ejike, 2007; Sastri, 1998).

Corrosion inhibitors from plant origin (roots, stems, leaves and seeds) are known to contain lone pair of electrons present on a hetero-atom ( i.e oxygen, phosphorous, sulphur and nitrogen), pi- bond, triple bond (e.g cyano group) in their functional group which are characteristics of a good corrosion inhibitor (Odiongenyi, 2006).

### **1.1. 2 Definition of Corrosion**

Corrosion is defined as the deterioration of materials by chemical interaction with the environment causing slow, steady and irreversible deterioration of the metal in both physical and chemical properties (Sastri, 1998). It is also defined as an electrochemical process by which metallic surfaces reacts with their environment causing the metal to lose its material properties due to surface deterioration (Boyanzier & Hammounti, 2004).

Virtually all metals with exception of gold and platinum corrode in an oxidizing environment forming compounds either in their oxides, hydroxides and sulphates (Ashworth, 1996; Nasa-Nasa, 1994; Vasant & Bansal, 2013). Corrosion causes important material and economical losses due to partial or total replacement of equipment and structures and plant repairing shutdowns (Fontana *et al.*, 1967; Sastri, 1998).

### 1.1.3 FORMS OF CORROSION

#### a) Classification by Mechanism

Corrosion can be classified into the following forms based on the chemistry of their occurrence.

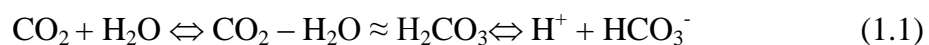
#### Sweet (CO<sub>2</sub>) Corrosion

Carbon dioxide corrosion, also called “sweet” corrosion, is often encountered in oil and gas production wells and is the main cause of material failures. There are three main reasons for this observed prevalence of CO<sub>2</sub> corrosion.

- i. The actual CO<sub>2</sub> corrosion mechanism itself is still not fully understood.
- ii. The existing long-term prediction models are unreliable.
- iii. The carbon and low-alloy steels, widely used in oil and gas production wells, have poor resistance against CO<sub>2</sub> corrosion (Kermani & Morshed, 2003).

Sweet corrosion is gaining additional attention due to the increased use of CO<sub>2</sub> injection method for enhanced oil recovery (EOR). Dry CO<sub>2</sub> gas is not corrosive at the temperatures occurring in oil and gas production wells and requires an aqueous phase. The main cause of the corrosion is that CO<sub>2</sub> dissolves in water, yielding a weak acid, H<sub>2</sub>CO<sub>3</sub> which can be corrosive (Kermani & Morshed, 2003).

The equilibrium makes it difficult to identify the rate-determining step (RDS) in the reaction between the dissolved CO<sub>2</sub> and the steel surface (Chukwudeme *et al.*, 2009)



Although CO<sub>2</sub> corrosion itself generally doesn't cause catastrophic failures, such as the cracking associated with H<sub>2</sub>S corrosion, its high corrosion rate can, in the end, be even more damaging. CO<sub>2</sub> corrosions often occur as general corrosion or localized corrosion, such as pitting, mesa-attack, and flow-induced localized corrosion, (Newton & Hausler, 1984).

### **Sour (H<sub>2</sub>S) Corrosion**

H<sub>2</sub>S reacts with steel to form a semi-protective film of iron sulfide (FeS). Because the FeS film is normally not uniform and can be removed by liquid flow, fresh metal is exposed to H<sub>2</sub>S. The exposed area is anodic and small in area compared to the surrounding iron sulfide film. Hence, the exposed metal preferentially corrodes causing pitting. When H<sub>2</sub>S concentrations are low, however, sulphide stress cracking (SSC), a form of hydrogen stress cracking (HSC), can occur (Felipe & Mize, 1994; Schroder *et al.*, 1999).

The role of H<sub>2</sub>S in SSC formation is to provide hydrogen at the metal surface by corrosion and to prevent hydrogen escaping into the surrounding fluid. In the absence of H<sub>2</sub>S, hydrogen normally formed at a cathode in a production well would simply bubble off. However, sulfide in surrounding fluids prevents the escape of hydrogen (H<sub>2</sub>S poison effect). The hydrogen thus finds an alternative path through the metal due to the small size of the hydrogen atom. At high temperatures the migration of the hydrogen atoms is rather easy; but, at low temperature migration is restricted and, therefore, the concentration of hydrogen atoms inside the metal (where temperature is lower than in the surrounding fluid) builds up (Bellarby, 2009).

### **Microbiologically Influenced Corrosion**

Microbiologically influenced corrosion (MIC) is also known as biocorrosion or microbial corrosion. It occurs when micro-organisms complicate matters in the environment. The type of metal used in construction, the microstructures, the metal surfaces, metal alloys, all

play a part in affecting MIC. An understanding of MIC requires an understanding not only of corrosion but of microbiology. Describing the types of corrosion, bacteria, algae and fungi all play a role; and the average dimensions of these microbes is typically in the range of micrometres. Their small size makes their dispersion in the environment and into crevices and many hard to access areas possible gives the definition of MIC as “The electrochemical process, here the participation of microorganisms, is able to facilitate, or accelerate the corrosion reactions without changing its electrochemical nature”(Videla, 1996).

Bacteria can be quite detrimental and to further complicate the problem they are able to withstand extreme conditions; often from below freezing to quite high temperatures. Another problematic characteristic they possess is their ability to enter a “spore” form once they are dehydrated together with their ability to remain in a spore stage until an acceptable environment allows them to germinate later(Borenstein, 1994). All natural waters contain bacteria and often MIC is observed in stagnant process waters.

Bacteria can work to instigate MIC in a number of ways:

- i. They can destroy protective films on the metals.
- ii. They can produce localized acid environments.
- iii. They can form corrosive environments.
- iv. They can alter anodic/ cathodic reactions.

**b)                   Physiochemical Classification**

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

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

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

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

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

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

**Corrosion via hydrogen Embrittlement and Blistering:** This is associated with the hydrogen atoms that can be produced on the metal surface in an aqueous medium, a reduction reaction occur when atomic hydrogen penetrates the metal. The presence of

defects allow the interaction between the hydrogen atoms and the metal forming molecular hydrogen which can be trapped by the metal producing enough pressure to form blisters resulting to micro-cracks. This occurs mainly in basic media where there are compounds such as sulphides or cyanide, (Hotlets *et al.*, 2007).

**Corrosion by Cavitation:** This is a form of corrosion caused by the formation and rupture of vapour bubbles in the fluid near the metal surface causing sequence of pits in the form of small but deep cracks (Ali & Folaud, 2012).

#### **1.1.4 CORROSION MEASUREMENT AND MONITORING.**

Corrosion monitoring is a series of quantitative method by which the effectiveness of corrosion control and prevention technique can be evaluated. The overall aim of monitoring corrosion is because it provides a feedback which enables corrosion control and prevention methods to be optimized. A variety of technique can be employed and they are:

**i) Non destructive testing:**

This includes use of ultrasound testing, radiography, thermography, eddy current / magnetic flux and intelligent pigs in measuring the effectiveness of a corrosion control and prevention technique (Devalapura *et al.*, 1994). It also involves pH measurement, dissolved gas (O<sub>2</sub>,CO<sub>2</sub> H<sub>2</sub>S) evaluation, metal count (Fe<sup>2+</sup>·Fe<sup>3+</sup>) determination, microbiological analysis in measuring the effectiveness of a corrosion control and prevention technique.

**ii) Operational Data :**

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

#### iv) **Fluid Electrochemistry**

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

##### **1.1.5. INHIBITORS**

Inhibitors are often considered to be the first line of defense against corrosion. NACE International states that an inhibitor is a substance which retards corrosion when added to an environment in small concentrations (Jones, 1988). Another generalization is that all inhibitors directly or indirectly coat or film the metal surface (Jones, 1988). In a broader view many different substances can be called inhibitors: Organic film formers (eg: Imidazolines/ amides, nitrogen heterocycles, fatty acid salts) such as:

Scavengers (sulphites for oxygen or aldehydes for hydrogen sulfide)

- i. Neutralizers ( simple amines)
- ii. Inorganic film formers ( phosphates or zinc/ calcium salts)
- iii. Passivators ( chromates or nitrites)
- iv. Bactericides (ex: aldehydes or quats)

An inhibitor can be said to function by either adsorbing onto the surface of a metal, thereby producing a thick corrosion product, or by changing the corrosive environment (Nathan & Bregman, 1973). Generally, inhibitors function by doing the following:

- i. Forming protective filming or scales
- ii. Slowing the corrosion rate by increasing/ decreasing the anodic/ cathodic reactions

- iii. Decreasing the diffusion rate of ions to the metal surface
- iv. Increasing the electrical resistance of the metal surface.

### **1.1.6 DRILLING FLUIDS**

Drilling fluid is a circulating fluid used in drilling to perform any or all of the various functions required in drilling operations. It is the single most essential system in safe, efficient, and economic well drilling. The drilling fluid consists of a mixture of natural and synthetic compounds used for a variety of purposes, Fink (2011).

The challenges met during drilling operations in the petroleum industry have led to the formulation of different types of drilling fluids. Drilling muds are classified based on the continuous phase of the mud and they include;

**a) Water Base Muds (WBM)** – Also referred to as aqueous drilling fluid. It is basically 90–95 % of fresh water, salt or sea water and several dissolved substances meaning that water is the continuous phase here (Skalle, 2010; Devereux, 1999). It is predominantly used in the industry due to its environmentally acceptable nature, and also because it is relatively cheap to operate with.

**b) Oil Base Muds (OBM)** – These muds have oil as their continuous phase, usually diesel oil, mineral oil or low toxicity mineral oil, and although they may pick up formation water, no additional water or brine is added. This is due to the fact that they contain water-emulsifying agents. This system which contains less than 5 % water has a number of advantages compared to WBM (Devereux, 1999).

## 1.2 Problem Statement

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

Corrosion of metals in a corroding environment is practically unavoidable because metals are thermodynamically unstable in the environment.

- i. Corrosion has over time proven a source of loss in drilling.
- ii. The use of corrosion inhibitors in mitigating the effect of corrosion in drilling remains expensive and yet environmentally unfriendly.

## 1.3 Objectives of Study

The main objective of this study is to use biomass inhibitor of plant origin as suitable substitutes to synthetic corrosion inhibitors used as additives to drilling fluid during oil drilling.

The specific objectives set out to achieve the aforementioned are as follows:

- i. To ascertain the inhibition efficacy of a synthetic corrosion inhibitor commonly used as an additive to drilling fluid in a simulated drilling fluid.
- ii. To ascertain the inhibition efficacy of the ethanol extracts of *chrysophyllum albidum* leaves in a simulated drilling fluid.
- iii. To investigate the effect of temperature on the corrosion rate and inhibition efficiencies of *chrysophyllum albidum* and synthetic corrosion inhibitor.
- iv. To determine some thermodynamic parameters from temperature studies involving the two inhibitors
- v. To determine the possible mechanism of the inhibition process of the above stated inhibitors.

#### **1.4 Justification of Study**

Plants extracts are organic inhibitors containing phytochemicals such as tannin, alkaloids, saponins and terpenoids with molecular & electronic structures similar to those of conventional corrosion inhibitors. The use of plant extracts as corrosion inhibitors pose immense benefits. Apart from minimizing cost, it has been proven to be more eco-friendly and generally less harmful to use. Furthermore these Organic inhibitors from natural products like other conventional inhibitors act by adsorbing on the metal surface to form an insoluble organic complex compound with the corroding specie hence reducing and preventing its attack on the metal surface.

#### **1.5 Scope of Study**

The scope of this study covers the assessment and comparison a synthetic corrosion inhibitor and an organic inhibitor of plant origin in the corrosion inhibition of mild steel in a simulated drilling fluid medium. Weight loss and potentiodynamic polarization techniques are applied in this study to monitor inhibiting effectiveness of the selected corrosion inhibitors. Electrochemical method (potentiodynamic polarization technique) was also carried out to determine some corrosion kinetic parameters such as corrosion current density,  $I_{\text{corr}}$ , corrosion electrode potential,  $E_{\text{corr}}$  and to determine the type of inhibitor from the polarization curves. Temperature studies was also carried out to determine some thermodynamic parameters such as activation energy, Gibb's free energy and change in enthalpy, hence, suggest the possible mechanism of the adsorption process

## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1. METALLIC CORROSION INHIBITOR OF PLANT ORIGIN

Corrosion inhibition of mild steel in 2 M HCl and 1 M H<sub>2</sub>SO<sub>4</sub> by extracts of selected plants was investigated by Oguzie (2008) using a gasometric technique at temperatures of 30 and 60 C. The studied plants materials include leaf extracts *Occimum viridis* (OV), *Telferia occidentalis* (TO), *Azadirachta indica* (AI) and *Hibiscus sabdariffa* (HS) as well as extracts from the seeds of *Garcinia kola* (GK). The results indicate that all the extracts inhibited the corrosion process in both acid media by virtue of adsorption and inhibition efficiency improved with concentration. Synergistic effects increased the inhibition efficiency in the presence of halide additives. Inhibition mechanisms were deduced from the temperature dependence of the inhibition efficiency as well as from assessment of kinetic and activation parameters that govern the processes. Comparative analysis of the inhibitor adsorption behaviour in 2 M HCl and 1 M H<sub>2</sub>SO<sub>4</sub> as well as the effects of temperature and halide additives suggest that both protonated and molecular species could be responsible for the inhibiting action of the extracts.

Plant extracts have been known to possess suitable phytochemicals which function as corrosion inhibitors. Pravinar *et al.* (1993) reported the inhibitive effect of aqueous extract of Eucalyptus leaves in the corrosion of mild steel and copper in 1M HCl solution. In his work, the inhibition efficiency was determined using galvanostatic polarization. He reported that the inhibition efficiency varied directly with concentration of the extract. He also reported on the decrease of inhibition efficiency with increase in temperature. The extract was found to be a mixed type inhibitor (i.e both cathodic and anodic reactions) predominantly of cathodic control.

El Hhosary *et al.* (1972) reported on the use of tobacco stems and leaves extracts as suitable corrosion inhibitors on aluminium and steel in a saline solution. Tobacco extract are reported to contain high concentration of chemical compounds including terpenes, alcohols, polyphenols, carboxylic acids, nitrogen containing compounds and alkaloids that exhibit electrochemical activity such as corrosion inhibition.

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

The inhibition efficacy of the aqueous extracts of the leaves of Henna *Lawsonia* on carbon, steel and zinc in both acidic and alkaline solution was reported by El-Etre *et al.* (2005). The report showed that the extracts were good corrosion inhibitor for the three metals in all tested media. The authors El –Etre *et al.* (2005) postulated that the degree of inhibition depended on the nature of the metal and the type of the medium. For steel and nickel, the inhibition efficiency increased in the order alkaline < neutral < acidic while in case of zinc it increased in order acid < alkaline < neutral thereby reconciling with observed concept of the Lawsonia extract being a mixed inhibitor. The inhibitive action of the extract was discussed in view of the adsorption of the complex Lawsonia molecules into the metal surface. El –Etre *et al.* (2005) found that this adsorption followed Langmuir adsorption isotherm in all tested systems. They also proposed that the formation of the complex between the metal cation and Lawsone (2 – hydroxyl -1, 4-naphthoquinone) was an additional inhibition mechanism of steel and nickel corrosion.

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

The effect of acetyl-eugenol, a derivative of eugenol on the corrosion inhibition of steel in 1M HCl solution was investigated by Chaieb *et al.* (2005) using weight loss, electrochemical impedance spectroscopy and electrochemical polarization methods. Results of the experiment showed that the extracts reduced corrosion rate of steel in 1M HCl significantly. Their inhibition efficiencies were found to increase with the inhibitor and attained 80 – 91% at concentration of 0.173g/L respectively. This implies that acetyeugenol is more active to the surface as compared to eugenol due to the presence of the carbonyl group. Similarly, the effect of temperature was also investigated at maximum concentration of both eugenol and acetyl eugenol at 0.173g/L. The result indicated that as the temperature increases the inhibitor performance changed from 64% at 298 K to 87% at 328 K. The adsorption of these extract on the metal surface was reported to follow Langmuir adsorption isotherm.

Lebe *et al.*(2014) researched on the inhibition of mild steel in HCl solution by *Pentaclethramacrophylla Benyham*(PMB) extract in 1M HCl using weight loss and electrochemical techniques (Open circuit potential, Linear sweep voltametry and potentiodynamic polarization) at 30 – 45<sup>0</sup>C revealed that *Pentaclethramacrophylla Bentham* extract retarded the dissolution of mild steel in 1 M HCl solution. The inhibition efficiencies obtained increased with increase in extract concentration as well as increase in temperature

which suggests physical and chemical adsorption mechanism. Open circuit potential shows reduction on resistance potential  $R_p$  with addition of the plant extract on the mild steel surface. Experimental data obtained fitted well with Langmuir and Temkin adsorption isotherm models. The mechanism of physisorption was proposed from the trend of inhibition efficiency with temperature obtained from experimental data.

The inhibitive and adsorption properties of ethanol extract of *Vernonia amygdalina* on the corrosion of mild steel in 0.2 - 0.5M  $H_2SO_4$  at 303 K using weight loss, thermometric, gasometric and IR methods of monitoring corrosion was investigated by Odiongenyi *et al.* (2008). His findings showed that the ethanol extracts of *Vernonia amygdalina* acted as good corrosion inhibitors on mild steel. The inhibition efficiency increased as the concentration of the extract increases. The inhibitor was also found to be a mixed type inhibitor and the adsorption of the inhibitor followed Langmuir adsorption isotherm. Phytochemical studies also revealed that ethanol extract of *Vernonia amygdalina* contain tannin, flavonoid and anthraquinone all contributing to the corrosion inhibition.

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

Al –Sebaibani (2000) worked on the inhibition efficacy of the water extracts of Henna leaves on mild steel in both alkaline and acidic medium. According to his findings, the extracts are good corrosion inhibitors whose maximum efficiency attained by just 200g/L of the extract was up to 96 % and observed no inhibition for steel and aluminium in NaCl solution.

The effect of naturally occurring extract of Artemisia on the corrosion of steel in 0.5M  $H_2SO_4$  in the temperature range of 298 K-353 K was studied using weight loss, electrochemical polarization and linear polarization methods by Bouklah and Hammouti (2006). The result obtained revealed that the extract reduces the corrosion rate quite significantly. The inhibition efficiency increases with the increase of Artemisia content at 10g/L to reach 95 % and 99 % at 298 K and 353 K respectively. The inhibition efficiency increased with temperature and it was found that the adsorption of Artemisia extract on the steel surface follows Langmuir adsorption isotherm. Similar result was investigated on the Artemisia oils on the corrosion of steel in HCl (Bendahou *et al.*, 2006; Bouklah & Hammouti, 2004). Artemisia was found to be a good and potent anti-malaria drug and divanone has been found to be its major constituent (Benjilali *et al.*, 1982). Since divanone is a diketone compound the inhibitory action was interpreted to be the formation of Fe(II) – Divanone complex.

Rehan (2003) conducted a research on the effect of the water extract from dry leaves of economic plants, date palm (*Phoenix dactylifera*), Henna (*Lawsonia inermis*) and corn (*Zea mays*) on the corrosion inhibition of commercial grade metals, steel, aluminum and copper in acidic chloride and sodium hydroxide solution using weight loss, solution analysis and potential measurements. The inhibition action was found to critically depend on the metal type and solution composition. Only date palm and henna extract were found highly

effective in reducing corrosion rate of steel in acidic chloride solutions. The inhibition efficiency increased with increasing concentration of the extract. The inhibition was interpreted in terms of chemisorptions of some active ingredients in the leaves according to Temkin isotherm. The leaves of date palm and corn are generally by-products and used chiefly in Basketry and animal feeding respectively. Henna leaves are used as hair dyestuff and in shampoo industry due to pleasant dermatological effect.

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

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

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

Iloamaeke *et al.* (2012) studied the Corrosion inhibition of mild steel using pterocarpussoyauxi, (PS) was studied using weight loss measurement at 30°C and 60°C. The inhibition efficiency increased with an increase in inhibitor concentration but decreased with temperature. The inhibition of corrosion of mild steel obeyed Tempkin and Freundlich adsorption isotherms and fitted into First Order reaction kinetics. Some thermodynamics parameters, such as  $E_a$ ,  $\Delta H$ , and  $\Delta G$ , were calculated and all indicated that inhibition of corrosion of mild steel by ethanol extract of PS was by Physical adsorption mechanism.

Yetri *et al.* (2014) investigated the Inhibition and adsorption properties of Theobroma cacao peel polar extract (TCPE) addition on corrosion inhibition efficiency of 0.3% C mild steel in hydrochloric acid solution for various exposing time, TCPE concentration and working temperature using weight loss test method. Electrochemical polarization test was also conducted to confirm the effectiveness of inhibition. Infrared spectrums of the samples were also evaluated to reveal compounds of the extract which control the inhibition process.

Morphology and local composition of sample surfaces were respectively examined by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX). Thermodynamic parameters such as energy activation, enthalpy, entropy and change in the free energy were then determined using related data. The result shows that the inhibition efficiency increases significantly up to 96.3% (by weight loss method) and 95.6% (by electrochemical polarization) with the increase of TCPE content. The optimum efficiency is obtained at TCPE concentration of 2.5% for exposing time of 768 h. However, the efficiency decreases slightly with increasing working temperature in the range of 303K-323K. The polarization curve shows the inhibitor behaves as a mixed inhibitor with the dominant cathodic inhibition. TCPE is identified to have functional groups of phenol, aromatic rings and ether. This compound is then adsorbed by the surface of the mild steel. The adsorption model is found to obey Langmuir adsorption isotherm. Surface condition is improved due to the adsorption and then formation of thin layer film protection in the surface of the steel. The addition of TCPE into HCl is effective to minimize corrosion attack on the mild steel.

Thilagavathy and Saratha (2015) investigated the corrosion inhibition efficiency of the acid extract of mirabilis jalapa flowers for the dissolution of mild steel in 1M HCl was studied at different concentrations of the extract, various immersion periods and at certain elevated temperatures. Data were fit into Langmuir and Temkin isotherms. Activation energy ( $E_a$ ), Entropy change ( $\Delta S$ ), Enthalpy change ( $\Delta H$ ) and Heat of adsorption ( $Q_{ads}$ ) were obtained from the Arrhenius plot. Nyquist and Bode plots were obtained to discuss the mode of inhibition and the inhibition efficiency was calculated from the electrochemical kinetic parameters.

Krishnaveni *et al.* (2013) Investigated corrosion inhibition of mild steel in hydrochloric acid medium using Morindatinctoria (MT) extract. The Morindatinctoria (MT) plant leaves extract was prepared in aqueous and hydrochloric acid media and was used as corrosion inhibitor for mild steel in hydrochloric acid medium. MT is found to be an efficient inhibitor at room temperature and the efficiency decreases with increase in temperature. Results from colorimetric studies predict the amount of iron present in the test solution and the percentage inhibition efficiency values calculated from this data fit well with the weight loss experiments. The AC impedance studies reveal that the mild steel surface is positively charged and the process of inhibition is through charge transfer. Polarisation studies indicate the mixed nature of the inhibitor. Thermodynamic parameters obtained predict that the process of inhibition is a spontaneous one.

The corrosion inhibition of mild steel in 1.0 M HCl by the Aloes leaves extract has been studied by Cang *et al.* (2013) using weight loss methods, potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The results show that the inhibition efficiency increases with the increase of the extract concentration. The effect of temperature on the corrosion behavior of mild steel in 1M HCl with addition of the extract was also studied. The adsorption of the extract molecules on the steel surface obeys Langmuir adsorption isotherm and occurs spontaneously. The activation energy as well as other thermodynamic parameters for the inhibition process was calculated. These thermodynamic parameters show strong interaction between inhibitor and mild steel surface.

Vasudha and Priya (2014) investigated the Inhibition efficiency of dry Polyalthialongifolia (Asoka tree) leaves on corrosion of mild steel in 1N H<sub>2</sub>SO<sub>4</sub> medium by weight loss and temperature studies. Effect of temperature (35-75 °C) on the corrosion behavior of mild steel in the presence of plant extract was studied. Inhibition was found to

increase with increase in concentration of the extract. Adsorption of extract molecules on mild steel surface obeyed the Langmuir, Temkin, Freundlich adsorption isotherms. Surface analysis was studied by SEM analysis. The results obtained prove that the leaves of *Polyalthia Longifolia* act as a good corrosion inhibitor having efficiency of 92% at 1.5% inhibitor concentration.

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

Buchweishaya and Mhinzi (2008) investigated the inhibition effect of gum exudates from *Acciaseyalvarseyalon* corrosion of mild steel in drinking water using electrochemical techniques (i.e potentiodynamic polarization and electrochemical impedance spectroscopy).

The Acacia gum exudates are obtained from stems and branches of sub-saharan Leguminosae trees which grow extensively in central Tanzania. These exudates particularly from Senegal are permitted food additive. It was found that *Acacia Seyal* var *Seyal* could serve as an effective green corrosion inhibitor for mild steel in drinking water systems. The percentage inhibition efficiency was found to increase with increasing concentration of the gum, the inhibition efficiency was almost unaffected by the change of solution temperature.

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

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

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

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

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

inhibitors. The adsorption of the inhibitors obeyed Langmuir and Freundlich adsorption isotherm.

## CHAPTER THREE

### MATERIALS AND METHOD

#### 3.1 MATERIALS

The experiments were carried out using the following apparatus and reagents: 500 ml Conical Flasks, Beakers, 2000 ml Round Bottom Flask, 1000 ml Volumetric Flask, Reflux Condenser, Measuring Cylinders, Water bath, Retort Stand, Wire gauze, Electronic Digital Weighing Balance, Electrical Hand Drier, EmryPaper, Ground African Star Apple Leaves (*Chrysophyllum albidum*), Synthetic Organic Inhibitor, 1 M  $H_2SO_4$  Solution, Simulated drilling fluid, Acetone and Ethanol

#### 3.2 Material Preparation

The mild steel used for the study was obtained from the Material and Metallurgical Workshop, Federal University of Technology Owerri. The mild steel had the following composition: Carbon 0.05, Silicon 0.3, Manganese 0.6, Phosphorous 0.36, the rest Iron. The sheets were mechanically press cut into 30 cm by 30 cm samples. These sheets were polished using different grades of emery papers, degreased in ethanol, dried in acetone and electrical hand drier before storing in a moisture free desiccator prior to use (Oguzie, 2008; Okafor *et al.*, 2008; Uwah *et al.*, 2012). The aggressive solution used was a simulated drilling fluid prepared with 1 M  $H_2SO_4$ . This was prepared by diluting 50g of bentonite powder and 1M sulphuric acid in 1000 cm<sup>3</sup> of water. The experiments were carried out in unstirred solutions and all weighing were done using electronic digital weighing balance.

### **3.3 Preparation of Inhibitors**

The synthetic inhibitor used for the study was purchased from a drilling firm in Port-Harcourt, Rivers State of Nigeria. The inhibitor is one of the additives added to Water Based Mud used for drilling. The concentrations of the Synthetic Inhibitor used for the study are 50 ml, 100 ml, 150 ml, 200 ml and 250 ml.

The leaves of *Chrysophyllum albidum* were collected from a local bush at Mpama-Egbu village in Owerri Municipal Local Government Imo State. These leaves were washed with distilled water, dried at room temperature to avoid loss of major organic component of the plant and ground to powder. 50 g of the powdered samples was extracted continually with 300 cm<sup>3</sup> of absolute ethanol in a soxhlet extractor for 4 hours. The concentrations of the extracts were calculated. From the stock solution, inhibition test solution was prepared to obtain 81.8 ml, 163.6 ml and 218.2 ml used for weight loss measurement.

### **3.4 Corrosion System**

The corrosive environments used for the study were the simulated drilling fluids with and without the inhibitors under study. The three media used are the Simulated Drilling Fluid, Simulated Drilling Fluid + ethanol extracts of *Chrysophyllum albidum* and the Simulated Drilling Fluid with Synthetic Inhibitor.

### **3.5 Experimental Set- Up and Monitoring**

#### **a) Weight loss measurement:**

Corrosion rates and inhibition efficiency were monitored using weight loss technique. The initial weights of the coupons were recorded to the nearest 0.0000 using electronic digital weighing balance. The coupons were totally immersed in a 300ml beaker with the aid

of a glass rod and a hook containing different prepared environment. The procedure was conducted with and without the various concentrations of the plant extract and the synthetic inhibitor after which the various coupons were withdrawn from the corrosive environment at different time intervals. These were then cleaned with ethanol and dried using acetone and electronic hand drier and then reweighed. The weight loss was taken as the difference in the weight of the specimen before and after immersion. The experiment was conducted in triplicate to ensure reliability of the result and the mean weight loss was reported (Oguzie, 2006; Okafor *et al.*, 2012; Uwah *et al.*, 2012).

The corrosion rate and inhibition efficiency is given by the equation

$$\text{Corrosion rate} = \frac{\text{Weight loss } \Delta W}{\text{Area} \times \text{Time}} \quad (3.1)$$

$$\Delta W = \text{Weight loss}$$

$$A = \text{Area of coupon}$$

$$T = \text{Time in hours}$$

$$\text{Inhibition efficiency (I.E)} = 1 - \frac{W_{inh}}{W_{blk}} \times 100 \quad (3.2)$$

Where  $W_{inh}$  = weight loss in inhibitor

$W_{blk}$  = weight loss in blank

### 3.6 Electrochemical Measurement

Electrochemical tests were conducted in a conventional three-electrode corrosion cell, using a V3 potentiostat/galvanostat, coupled to a PC, running on the Powersuite and Powersine software. A graphite rod and saturated calomel electrode (SCE) served as counter

and reference electrodes respectively. Test metal specimens were fixed in epoxy resin with a surface area of 1 cm<sup>2</sup> exposed to the test solution. Measurements were in aerated and unstirred solutions at the end of 1800s of immersion at 30±1 °C. Each test was run in triplicate and the mean values of the measured parameters presented.

Potentiodynamic polarization measurements were performed at a scan rate of 0.333 mV/s and potential range ±250 mV versus corrosion potential. From the polarization curves, Tafel slopes, corrosion potential and corrosion current were analyzed using computer software, Ashassi – Sorkhabi & Seifzadeh (2006). The inhibition efficiency was calculated using Tafel method according to the equation below:

$$\text{Inhibition Efficiency (\%)} = \frac{I_{\text{corr (blank)}} - I_{\text{corr (inh)}}}{I_{\text{corr (blank)}}} \quad (3.3)$$

Where

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

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

### 3.7 Temperature Studies

Temperature studies were carried out by immersing pre- weighed coupons in 300ml beakers each of the blank and the test solutions of two different concentration (highest and lowest) at 313 K, 323K and 333K in a thermostat controlled water bath for three hours . The specimen were taken out, air dried and re-weighed. From the study, the weight loss, inhibition efficiency and corrosion rate were determined by applying the mathematical model stated in equation 1 and 2 above. Thermodynamic parameters were also obtained from experimental data. The activation energy of adsorption process was calculated using Arrhenius equation stated as follows

$$\ln \frac{CR_2}{CR_1} = \frac{Ea}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (3.4)$$

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

Gibb's free energy of reaction was also calculated using the relationship between equilibrium constant of the adsorption ( $K_{ads}$ ) of ethanol extract of *Chrysophyllum albidum* and synthetic inhibitor and the Gibb's free energy stated as follows

$$\Delta G = -2.303 RT \log (55.5K_{ads}) \quad (3.5)$$

Where  $K_{ads}$  the adsorption constant expressed as follows:

$$K_{ads} = \frac{\theta}{C_{inh}(1-\theta)} \quad (3.6)$$

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

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

$$Q_{ads} = 2.303R \left[ \log\left(\frac{\theta}{1-\theta_2}\right) - \log\left(\frac{\theta}{1-\theta_1}\right) \right] \times \frac{T_1 T_2}{T_2 - T_1} \quad (3.7)$$

Where  $\theta_1$  and  $\theta_2$  are the degree of surface coverage at temperature  $T_1$  and  $T_2$  and  $R$  is the rate constant.

**CHAPTER FOUR**  
**RESULTS AND DISCUSSION**

**4.1 Results**

Weight loss analysis was carried out on mild steel coupons in a simulated drilling mud at different concentrations of the ethanol extracts of CA and SI.

Tables 4.1 shows the gravimetric data in the absence and presence of the ethanol extracts of CA after 1 day.

**Table 4.1: Weight loss, corrosion rate (mdd), inhibition efficiency values of mild steel corrosion in a Simulated Drilling Fluid with and without Ethanol Extract of CA after 1 day**

<b>System</b>	<b>Initial Weight(g)</b>	<b>Final Weight(g)</b>	<b>Weight loss(g)</b>	<b>Average weight Loss(g)</b>	<b>Area of coupon (cm<sup>2</sup>)</b>	<b>Corrosion Rate (mdd)</b>	<b>Inhibition Efficiency (%)</b>
<b>Blank</b>							
A	3.4124	1.7849	1.6275	1.6277	0.16714	9.7385	-----
B	3.4454	1.8175	1.6279				
C	3.4562	1.8285	1.6277				
<b>81.8ml/L</b>							
A	3.4425	3.0435	0.3990	0.3989	0.16714	2.3866	75.4
B	3.4758	3.0770	0.3988				
C	3.5624	3.1635	0.3989				
<b>163.6ml/L</b>							
A	3.3033	3.1549	0.1484	0.1483	0.16714	0.8867	90.9
B	3.4022	3.2546	0.1476				
C	3.4565	3.3076	0.1489				
<b>218.2ml/L</b>							
A	3.2546	3.1535	0.1011	0.0996	0.16714	0.5959	93.88
B	3.4756	3.3791	0.0965				
C	3.4444	3.3432	0.1012				

From Table 4.1, it is obvious that the average weight loss decreased with increase in concentration of ethanol extract of CA in the simulated drilling fluid. It can also be seen that the highest weight loss was recorded in the absence of the ethanol extracts of CA.

The corrosion rate was found to be highest in the absence of the ethanol extracts of CA and decreased as the concentration of the inhibitor increased whereas the inhibition efficiency increased as the concentration of the ethanol extracts of CA increased.

The gravimetric data for the absence and presence of the ethanol extracts of CA measured after 2 days is represented in Table 4.2.

**Table 4.2: Weight loss, corrosion rate (mdd), inhibition efficiency values of mild steel corrosion in a Simulated Drilling Fluid with and without Ethanol Extract of CA after 2 days.**

System	Initial Weight(g)	Final Weight(g)	Weight loss(g)	Average weight Loss(g)	Area of coupon (cm <sup>2</sup> )	Corrosion Rate (mdd)	Inhibition Efficiency (%)
Blank							
A	3.3333	1.2257	2.1076	1.9726	0.16714	5.9010	-----
B	3.4878	1.6502	1.8376				
C	3.5678	1.5952	1.9726				
81.8ml/L							
A	3.2457	2.8449	0.4008	0.4010	0.16714	1.1996	79.6
B	3.5474	3.1460	0.4014				
C	3.7425	3.3417	0.4008				
163.6ml/L							
A	3.3325	3.1800	0.1525	0.1517	0.16714	0.4538	92.3
B	3.4527	3.3013	0.1514				
C	3.5555	3.4043	0.1512				
218.2ml/L							
A	3.4010	3.2956	0.1054	0.1052	0.16714	0.3147	94.6
B	3.5000	3.3954	0.1046				
C	3.2456	3.1400	0.1056				

Results obtained from weight loss measurement on the anticorrosion performance of the ethanol extracts of *Chrysophyllum albidum* (CA) in the simulated drilling fluid after 2 days as represented in Table 4.2 show that the average weight loss decreased with increase in concentration of ethanol extract of CA in the simulated drilling fluid. It can also be seen that the highest weight loss was recorded in the absence of the ethanol extracts of CA.

The corrosion rate was found to be highest in the absence of the ethanol extracts of CA and decreased as the concentration of the inhibitor increased whereas the inhibition efficiency increased as the concentration of the ethanol extracts of CA increased.

Table 4.3 summarises the gravimetric results in the presence and absence of the ethanol extracts of CA measured after 3 days.

Results shown on Table 4.3 which represents the anticorrosion performance of the ethanol extracts of *Chrysophyllum albidum* (CA) in the simulated drilling fluid after 3 days show that the average weight loss decreased with increase in concentration of ethanol extract of CA in the simulated drilling fluid. It can also be seen that the highest weight loss was recorded in the absence of the ethanol extracts of CA.

The corrosion rate was found to be highest in the absence of the ethanol extracts of CA and decreased as the concentration of the inhibitor increased whereas the inhibition efficiency increased as the concentration of the ethanol extracts of CA increased.

**Table 4.3: Weight loss, corrosion rate (mdd), inhibition efficiency values of mild steel corrosion in a Simulated Drilling Fluid with and without Ethanol Extract of CA after 3 days.**

System	Initial Weight(g)	Final Weight(g)	Weight loss(g)	Average weight Loss(g)	Area of coupon (cm <sup>2</sup> )	Corrosion Rate (mdd)	Inhibition Efficiency (%)
Blank							
A	3.3321	1.1150	2.2171	2.2179	0.16714	4.4232	-----
B	3.3487	1.1299	2.2188				
C	3.6547	1.4369	2.2178				
81.8ml/L							
A	3.3356	2.9131	0.4225	0.4215	0.16714	0.8406	80.9
B	3.4578	3.0369	0.4209				
C	3.2557	2.8346	0.4211				
163.6ml/L							
A	3.2587	3.1021	0.1566	0.1570	0.16714	0.3131	92.9
B	3.5468	3.3894	0.1574				
C	3.4217	3.2647	0.1570				
218.2ml/L							
A	3.4256	3.3184	0.1072	0.1074	0.16714	0.2142	95.15
B	3.5687	3.4614	0.1073				
C	3.2256	3.1179	0.1077				

**Table 4.4: Weight loss, corrosion rate (mdd), inhibition efficiency values of mild steel corrosion in a Simulated Drilling Fluid with and without Ethanol Extract of CA after 4 days.**

System	Initial Weight(g)	Final Weight(g)	Weight loss(g)	Average weight Loss(g)	Area of coupon (cm <sup>2</sup> )	Corrosion Rate (mdd)	Inhibition Efficiency (%)
Blank							
A	3.4121	0.8856	2.5265	2.5265	0.16714	3.7790	---
B	3.3325	0.8065	2.5260				
C	3.4242	0.8972	2.5270				
81.8ml/L							
A	3.2679	2.8450	0.4229	0.4231	0.16714	0.6329	81.2
B	3.3435	2.9199	0.4236				
C	3.2214	2.7986	0.4228				
163.6ml/L							
A	3.4760	3.3134	0.1626	0.1630	0.16714	0.2438	93.5
B	3.3478	3.1846	0.1632				
C	3.2587	3.0955	0.1632				
218.2mg/L							
A	3.4522	3.3438	0.1084	0.1081	0.16714	0.1617	95.7
B	3.3681	3.2603	0.1078				
C	3.2214	3.1133	0.1081				

Results summarized in Table 4.4 which shows the weight loss measurement on the anticorrosion performance of the ethanol extracts of *Chrysophyllum albidum* (CA) in the simulated drilling fluid after 4 days show that the average weight loss decreased with increase in concentration of ethanol extract of CA in the simulated drilling fluid. It can also be seen that the highest weight loss was recorded in the absence of the ethanol extracts of CA.

The corrosion rate was found to be highest in the absence of the ethanol extracts of CA and decreased as the concentration of the inhibitor increased whereas the inhibition efficiency increased as the concentration of the ethanol extracts of CA increased.

The result of the gravimetric studies in the presence and absence of the ethanol extracts of CA after 5 days is represented in Table 4.5

**Table 4.5. Weight loss, corrosion rate (mdd), inhibition efficiency values of mild steel corrosion in a Simulated Drilling Fluid with and without Ethanol Extract of CA after 5 days.**

System	Initial Weight(g)	Final Weight(g)	Weight loss(g)	Average weight Loss(g)	Area of coupon (cm <sup>2</sup> )	Corrosion Rate (mdd)	Inhibition Efficiency (%)
Blank							
A	3.1162	0.3902	2.7260	2.7266	0.16714	3.2627	-----
B	3.1304	0.4030	2.7274				
C	3.2232	0.4968	2.7264				
81.8ml/L							
A	3.4082	2.9722	0.4360	0.4363	0.16714	0.5220	84.04
B	3.3176	2.8813	0.4363				
C	3.2546	2.8180	0.4366				
163.6ml/L							
A	3.3402	3.1764	0.1638	0.1636	0.16714	0.1958	94.9
B	3.2337	3.0707	0.1630				
C	3.2555	3.0915	0.1640				
218.2ml/L							
A	3.1052	2.9959	0.1093	0.1090	0.16714	0.1304	96.6
B	3.2381	3.1294	0.1087				
C	3.2345	3.1255	0.1090				

Results represented in Table 4.5 above shows weight loss measurement on the anticorrosion performance of the ethanol extracts of *Chrysophyllum albidum* (CA) in the simulated drilling fluid after 5 days show that the average weight loss decreased with increase in concentration

of ethanol extract of CA in the simulated drilling fluid. It can also be seen that the highest weight loss was recorded in the absence of the ethanol extracts of CA.

The corrosion rate was found to be highest in the absence of the ethanol extracts of CA and decreased as the concentration of the inhibitor increased whereas the inhibition efficiency increased as the concentration of the ethanol extracts of CA increased.

The gravimetric studies of the presence and absence of the Synthetic Inhibitor in the simulated drilling fluid measured after 1 day is shown in Table 4.6

**Table 4.6. Weight loss, corrosion rate(mdd), inhibition efficiency values of mild steel corrosion in a Simulated Drilling Fluid with and without the Synthetic Inhibitor after 1 day.**

System	Initial Weight(g)	Final Weight(g)	Weight loss(g)	Average weight Loss(g)	Area of coupon (cm <sup>2</sup> )	Corrosion Rate (mdd)	Inhibition Efficiency (%)
Blank							
A	3.4423	2.3752	1.5047	1.5974	0.16714	9.5573	-----
B	3.4024	1.7121	1.6901				
C	3.2548	1.6574	1.5974				
50ml/L							
A	3.5218	3.3618	0.1600	0.1521	0.16714	0.9100	90.47
B	3.4456	3.3016	0.1440				
C	3.4422	3.2899	0.1523				
100ml/L							
A	3.3125	3.1747	0.1378	0.1401	0.16714	0.8382	91.23
B	3.4478	3.3052	0.1426				
C	3.6645	3.5246	0.1399				
150ml/L							
A	3.4785	3.3484	0.1301	0.1287	0.16714	0.7700	91.94
B	3.3047	3.1774	0.1273				
C	3.2546	3.1259	0.1287				
200ml/L							
A	3.4000	3.2883	0.1117	0.1115	0.16714	0.6671	93.0
B	3.4547	3.3437	0.1110				
C	3.2666	3.1548	0.1118				
250ml/L							
A	3.4256	3.3456	0.0800	0.0777	0.16714	0.4649	95.13
B	3.3629	3.3875	0.0754				
C	3.7777	3.7000	0.0777				

Results shown on Table 4.6 showing the weight loss measurement on the anticorrosion performance of the synthetic inhibitor in the simulated drilling fluid after 1 day show that the average weight loss decreased with increase in concentration the SI in the simulated drilling fluid. It can also be seen that the highest weight loss was recorded in the absence of the synthetic inhibitor.

The corrosion rate was found to be highest in the absence of the synthetic inhibitor and decreased as the concentration of the inhibitor increased whereas the inhibition efficiency increased as the concentration of the synthetic inhibitor increased.

**Table 4.7: Weight loss, corrosion rate (mdd), inhibition efficiency values of mild steel corrosion in a Simulated Drilling Fluid with and without the Synthetic Inhibitor after 2 days.**

System	Initial Weight(g)	Final Weight(g)	Weight loss(g)	Average weight Loss(g)	Area of coupon (cm <sup>2</sup> )	Corrosion Rate (mdd)	Inhibition Efficiency (%)
Blank							
A	3.3602	1.4055	1.9547	1.9999	0.16714	5.9827	-----
B	3.4112	1.3661	2.0451				
C	3.2256	1.2257	1.9999				
50ml/L							
A	3.5124	3.3433	0.1691	0.1702	0.16714	0.5092	91.49
B	3.4178	3.2470	0.1708				
C	3.4440	3.2733	0.1707				
100ml/L							
A	3.3354	3.1868	0.1486	0.1484	0.16714	0.4439	92.58
B	3.4170	3.2688	0.1482				
C	3.6655	3.5171	0.1484				
150ml/L							
A	3.6021	3.4710	0.1311	0.1308	0.16714	0.3913	93.50
B	3.3547	3.5241	0.1306				
C	3.2544	3.1237	0.1307				
200ml/L							
A	3.4578	3.3458	0.11200.1121	0.16714	0.3353	94.40	
B	3.4457	3.3338	0.1119				
C	3.2226	3.1102	0.1124				
250ml/L							
A	3.4789	3.3977	0.0812	0.0814	0.16714	0.2435	95.93
B	3.3625	3.2808	0.0817				
C	3.6641	3.5828	0.0813				

Table 4.7 shows the weight loss measurement on the anticorrosion performance of the synthetic inhibitor in the simulated drilling fluid after 2 days. It reveals that the average weight loss decreased with increase in concentration the SI in the simulated drilling fluid. It can also be seen that the highest weight loss was recorded in the absence of the synthetic inhibitor.

The corrosion rate was found to be highest in the absence of the synthetic inhibitor and decreased as the concentration of the inhibitor increased whereas the inhibition efficiency increased as the concentration of the synthetic inhibitor increased.

Table 4.8 shows the gravimetric measurements in the simulated drilling mud with and without the Synthetic Inhibitor after a period of 3 days.

**Table 4.8. Weight loss, corrosion rate (mdd), inhibition efficiency values of mild steel corrosion in a Simulated Drilling Fluid with and without the Synthetic Inhibitor after 3 days.**

System	Initial Weight(g)	Final Weight(g)	Weight loss(g)	Average weight Loss(g)	Area of coupon (cm <sup>2</sup> )	Corrosion Rate (mdd)	Inhibition Efficiency (%)
Blank							
A	3.2650	1.0671	2.1979	2.2179	0.16714	4.4232	-----
B	3.3890	1.1422	2.2378				
C	3.2568	1.0388	2.2180				
50ml/L							
A	3.4420	3.2662	0.1755	0.1751	0.16714	0.3492	92.11
B	3.2291	3.0543	0.1748				
C	3.4244	3.2494	0.1750				
100ml/L							
A	3.4117	3.2605	0.1512	0.1508	0.16714	0.3008	93.2
B	3.3779	3.2277	0.1502				
C	3.2555	3.1045	0.1510				
150ml/L							
A	3.6362	3.5011	0.1351	0.1351	0.16714	0.2694	93.88
B	3.3821	3.2471	0.1350				
C	3.4444	3.3092	0.1352				
200ml/L							
A	3.5066	3.3917	0.1149	0.115	0.16714	0.2295	93.9
B	3.4207	3.3050	0.1153				
C	3.6544	3.5400	0.1144				
250ml/L							
A	3.4444	3.3574	0.0870	0.0875	0.16714	0.1745	96.05
B	3.3416	3.2537	0.0879				
C	3.2627	3.1753	0.0875				

Table 4.8 shows the weight loss measurement on the anticorrosion performance of the synthetic inhibitor in the simulated drilling fluid after 3 days. It is obvious that the average weight loss decreased with increase in concentration the SI in the simulated drilling fluid. It can also be seen that the highest weight loss was recorded in the absence of the synthetic inhibitor.

The corrosion rate was found to be highest in the absence of the synthetic inhibitor and decreased as the concentration of the inhibitor increased whereas the inhibition efficiency increased as the concentration of the synthetic inhibitor increased.

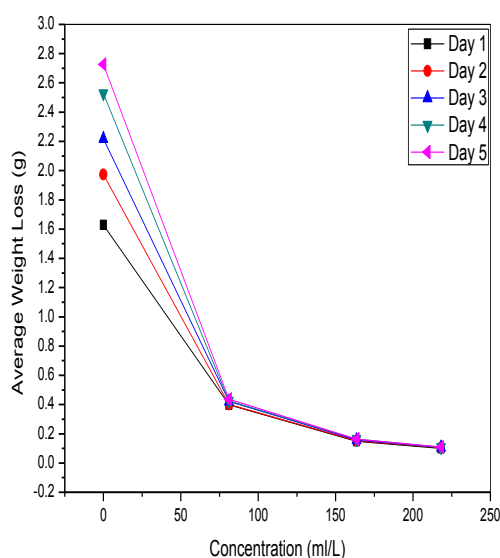
## 4.2 Analysis of Results from Gravimetric Measurement

Results obtained from weight loss measurement on the inhibition effect of *Chrysophyllum albidum*(CA) and the Synthetic Inhibitor (SI) on mild steel corrosion in a simulated drilling fluid as shown in Tables 4.0 – 4.8 above revealed the following:

### 4.2.1 Variation of Average Weight Loss with Various Concentrations of CA and SI in the Simulated Drilling Fluid

From the results on tables 4.0-4.8 above, it was shown that the average weight loss decreased with increase in the concentration of the ethanol extracts of CA and SI in the simulated drilling fluid. The tables also show that the highest weight loss was recorded in the absence of both corrosion inhibitors studied.

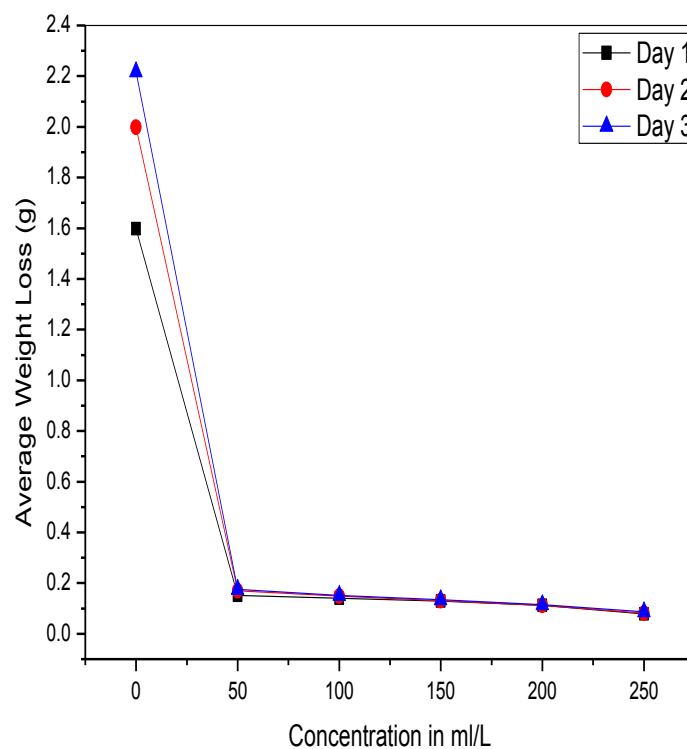
Figure 4.1 shows the variation of weight loss with various concentration of CA in the Simulated Drilling Fluid after Days 1, 2, 3, 4 and 5.



**Figure 4.1. Variation of weight loss with various concentration of CA in the Simulated Drilling Fluid after Days 1, 2, 3, 4 and 5.**

Weight loss decreased with increase in the concentration of the ethanol extracts of CA in the simulated drilling fluid. Highest weight loss was recorded in the absence of the plant extracts while as the concentration of the plant extracts was increased, weight loss decreased.

The variation of weight loss with various concentration of SI in the Simulated Drilling Fluid after Days 1, 2, and 3 days is shown on Figure 4.2.

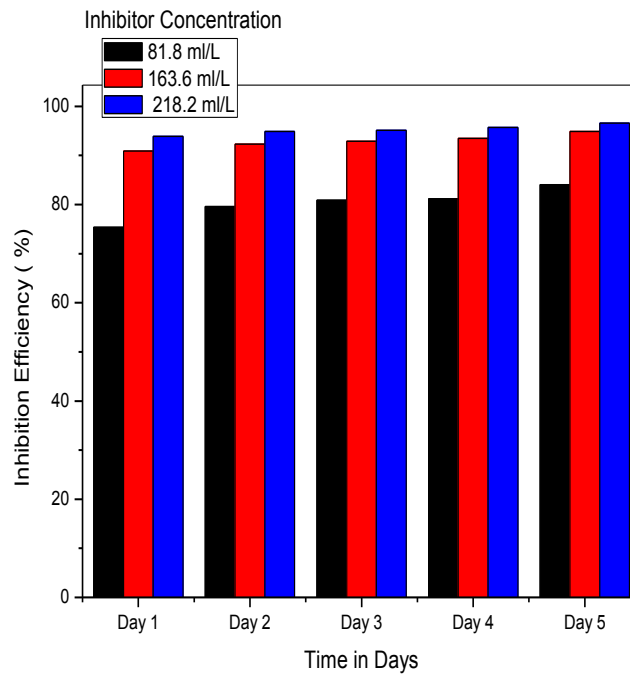


**Figure 4.2: Variation of weight loss with various concentration of SI in the Simulated Drilling Fluid after Days 1, 2 and 3.**

Weight loss decreased with increase in the concentration of the ethanol extracts of CA in the simulated drilling fluid. Highest weight loss was recorded in the absence of the plant extracts while as the concentration of the plant extracts was increased, weight loss decreased.

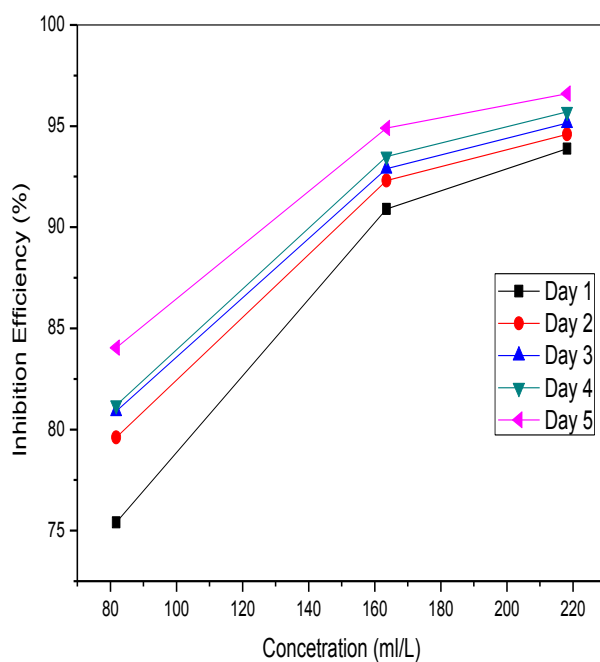
#### 4.2.2: Variation of Inhibition Efficiency with Immersion Time and with Concentration of CA and SI.

Tables 4.0- 4.9 above and Figures 4.5 - 4.8 summarize the variation between the inhibition efficiencies with concentration of the two inhibitors and with immersion time.



**Figure 4.5: Variation of Inhibition Efficiency with Immersion Time of Mild Steel in the Simulated Drilling Fluid at different Inhibitor Concentrations of CA**

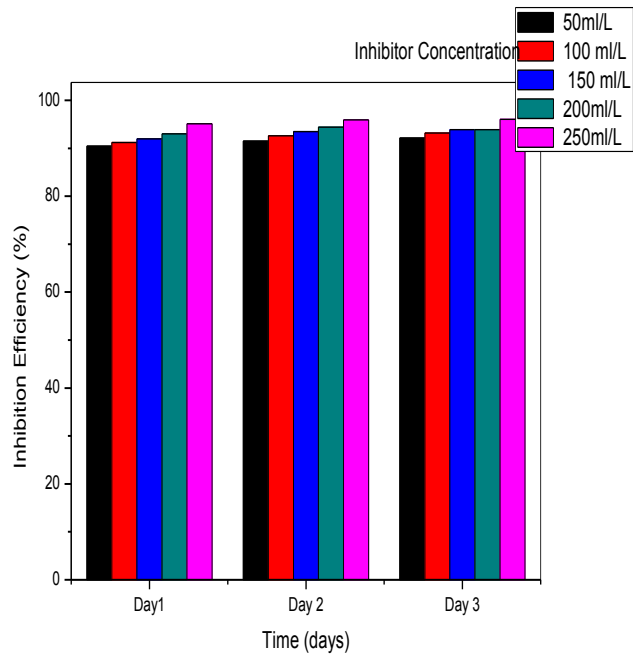
From Figure 4.5, it is seen that the inhibition efficiency of the CA in the simulated drilling fluid increased as time increase. The result obtained was consistent over the five day period studied.



**Figure 4.6: Variation of Inhibition Efficiency with Concentrations of CA at varying Immersion Time in the Simulated Drilling Fluid**

The inhibition efficiency of the CA in the simulated drilling fluid increased as the concentration of the ethanol extract of CA increased as shown in Figure 4.6.

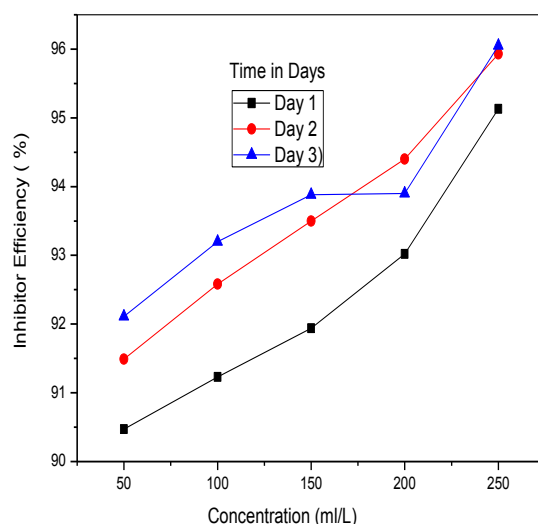
Figure 4.7 represents the variation of Inhibition Efficiency with Immersion Time of Mild Steel in the Simulated Drilling Fluid at different Inhibitor Concentrations of SI.



**Figure 4.7: Variation of Inhibition Efficiency with Immersion Time of Mild Steel in the Simulated Drilling Fluid at different Inhibitor Concentrations of SI**

It can be seen clearly from Figure 4.7 that the inhibitor efficiency increased very marginally with increased in time.

Figure 4.8 shows the variation of Inhibition Efficiency with different Inhibitor Concentrations of SI in the Simulated Drilling Fluid at varying Immersion Time of Mild Steel.



**Figure 4.8: Variation of Inhibition Efficiency with different Inhibitor Concentrations of SI in the Simulated Drilling Fluid at varying Immersion Time of Mild Steel**

Figure 4.8 above clearly shows that the inhibitor efficiency increased with increase in the concentration of the SI.

### 4.3 Analysis of Result from potentiodynamic polarization measurements

#### 4.3.1 Potentiodynamic polarization measurements for CA

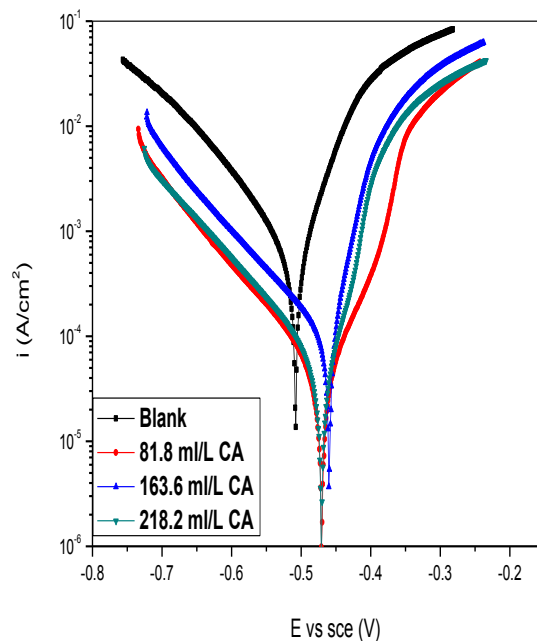
Polarization experiment was carried out to ascertain the effect of the CA extract on the cathodic and anodic half reactions. The effect of various concentrations of CA extract on the electrochemical corrosion behaviour of mild steel in the simulated drilling fluid was determined.

The polarization curves of mild steel in the simulated drilling fluid containing different concentrations of the inhibitor at 30°C is shown in Figure 4.9 above. The mild steel specimen dissolved actively with no distinctive transition to passivation within the studied potential range ( $\pm 250$  mV) in the corrosive environment. The effect of CA extract on  $E_{\text{corr}}$  was not significant though a slight shift was observed towards the anodic direction. Also, a

reduction in the cathodic and anodic half reactions was observed with predominant anodic effect. This therefore implies that the CA extract is a mixed type inhibitor. Though, CA extract functions as a mixed-type inhibitor with predominant anodic effect in the studied environment, the inhibition were concentration dependent. The values of the corrosion current density in the absence ( $i_{corr,bl}$ ) and presence of inhibitor ( $i_{corr,inh}$ ) were used to estimate the inhibition efficiency from polarization data (IE%) as follows:

$$IE\% = \left( \frac{I_{corr(bl)} - I_{corr(inh)}}{I_{corr(bl)}} \right) \times 100 \quad (4.1)$$

Where  $I_{corr(bl)}$  and  $I_{corr(inh)}$  represents the corrosion current density in the absence and presence of the inhibitor, respectively. It is clear that this result is in line with the gravimetric findings.



**Figure 4.9.** Potentiodynamic polarization curves of mild steel in the simulated drilling fluid in the absence and presence of various concentrations of CA.

**Table 4.9:** Polarization Parameters for Mild Steel in the Simulated Drilling Fluid in the Absence and Presence of CA.

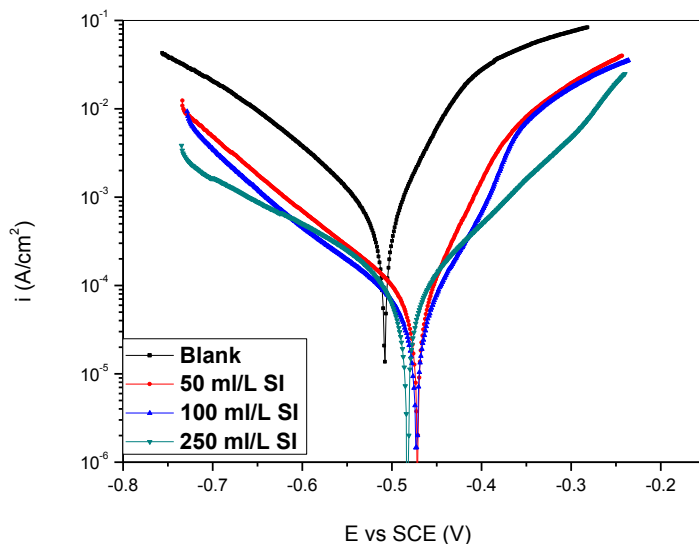
<b>System</b>	<b>E<sub>corr</sub></b> <b>(mV vs SCE)</b>	<b>I<sub>corr</sub></b> <b>(μA cm<sup>-2</sup>)</b>	<b>IE (%)</b>
<b>Simulated Drilling Fluid</b>	<b>- 521</b>	<b>605.4</b>	
81.8 ml/L CA	- 465.3	126.8	79.1
163.6 ml/L CA	- 461.7	45.6	92.5
218.2ml /L CA	- 473.2	13.7	97.8

#### 4.3.2 Potentiodynamic polarization measurements for SI

Potentiodynamic polarization test was carried out to determine the inhibiting effect of the SI on the anodic and cathodic half reactions. Figure 4.10 shows typical polarization curves for mild steel specimens in the simulated drilling fluid, in the absence and presence of different concentrations of SI. Accordingly, the metal specimen in the studied environment also showed active dissolution, no sign of passivation was observed within the studied potential range ( $\pm 250$  mV). Electrochemical constants, such as, corrosion potential ( $E_{corr}$ ), and corrosion current density ( $I_{corr}$ ), were as well obtained and their values are given in Table 4.10.

Results above show that in the test environment, the  $I_{corr}$  decreases in the presence of the inhibitor compared to the uninhibited solution. The polarization curves in presence of SI show evidence of inhibition. In the studied environment, SI has a slight effect on  $E_{corr}$ , this shifted towards the anodic direction, just like what was observed in the presence of CA, however, a shift of both the cathodic and anodic

curves towards lower corrosion current densities was noticed in the test environment, hence SI is regarded as a mixed type inhibitor.



**Figure 4.10.** Potentiodynamic polarization curves of mild steel in the absence and presence of various concentrations of SI.

**Table 4.10:** Polarization Parameters for Mild Steel in the Simulated Drilling Fluid in the Absence and Presence of SI

System	$E_{corr}$ (mV vs SCE)	$I_{corr}$ ( $\mu A\ cm^{-2}$ )	IE (%)
<b>Simulated Drilling Fluid</b>	<b>- 521</b>	<b>605.4</b>	
50 ml/L SI	-468.3	48.2	92.1
100 ml/L SI	-458.5	40.7	93.3
250 ml/L SI	-457.1	10.6	98.2

#### 4.4 Discussion of Results from Gravimetric Studies

Figures 4.5 and 4.7 illustrate the variation of inhibition efficiency with immersion time of mild steel in CA and SI respectively. It reveals an increase in inhibition efficiency with increase in immersion time of CA and SI in the simulated drilling fluid. Highest inhibition efficiency of 96.6% was observed after five days for CA and 96.05% was observed after three days for SI while lowest inhibition efficiency was recorded after twenty-four hours in both CA and SI.

The effect can be attributed to the fact that at longer immersion time the phyto-consituents present are more adsorbed and forms stronger co-ordinate bond with the metal surface at the metal solution interphase; formation of the insoluble protective film of organic complex is thus more enhanced resulting to greater surface coverage, hence, inhibition efficiency increases (Oguzie *et al.*, 2007; Okafor *et al.*, 2008). Similar results were obtained by Oguzie (2006).

Figures 4.6 and 4.8 illustrate the variation of inhibition efficiency with concentration of CA and SI respectively. It also reveals an increase in inhibition efficiency with increase in concentration of CA and SI in the simulated drilling fluid. Highest inhibition efficiency of 96.6% in CA at 218.2ml/L was observed and 96.05% in SI at 250ml/L was observed.

The effect indicates strong adsorption of the phyto-consituent present in CA and SI on the surface of the mild steel at higher concentration at the metal solution interphase. Surface coverage increases and the metal surface is more protected from corrosion. The result is consistent with the works of (Oguzie *et al.*, 2010; Raja *et al.*, 2009).

#### 4.5 Discussion of Results from Potentiodynamic Polarization Studies

Polarization results showed that corrosion current density ( $I_{\text{corr}}$ ) was lower at high concentration and higher at low concentration in both test media. This can be attributed to the increase in the block fraction of the metal surface by adsorption. Similar results have been obtained in works carried out by Oguzie *et al* 2010 and Sharmila *et al.*, 2010). The inhibition efficiency obtained from corrosion current density showed higher inhibition efficiency at high concentrations of both corrosion inhibitors under study than at lower concentration.

#### 4.6. Adsorption Considerations

Adsorption isotherms are essential in explaining the interactions between the inhibitor and the mild steel surface. Adsorption can be categorized into two based on the forces of attraction between the adsorbate and the adsorbent. These are: physical adsorption and chemical adsorption.

i. **Physical adsorption:**

This occurs when the force of attraction between adsorbate and adsorbent is Van der Waals force. In physical adsorption the force of attraction between adsorbent and adsorbate is very weak thus can easily be reversed by heating or increasing the pressure.

ii. **Chemical adsorption**

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

Different adsorption isotherm such as Langmuir, Temkin, Frumkin, Freundlich, Flory Huggins etc. can be used to explain adsorption process. The adsorption isotherms describes the behaviour of the aqueous plant extract on mild steel surface. The

correlation coefficient  $R^2$  is used to choose the isotherm that best fits experimental data.

In this work Langmuir adsorption was used to describe the adsorption process.

#### 4.7 Langmuir Adsorption Isotherm

Langmuir adsorption isotherm is an adsorption model which was published in 1916. The adsorption isotherm is based on the assumption that all adsorption sites are equivalent and that particles occur independently from nearby sites being occupied or not (Deng & Fu, 2012). The isotherm is based on four assumptions:

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

The degree of surface coverage ( $\theta$ ) values for different concentration of the inhibitors (CA and SI) in the simulated drilling fluid have been evaluated from weight loss data and is shown in Tables 4.11 – 4.12, using the mathematical model shown below (Morettif & Guidi, 2002):

$$\theta = 1.E(\%)/100 \quad (4.2)$$

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

$$C/\theta = 1/K + C \quad (4.3)$$

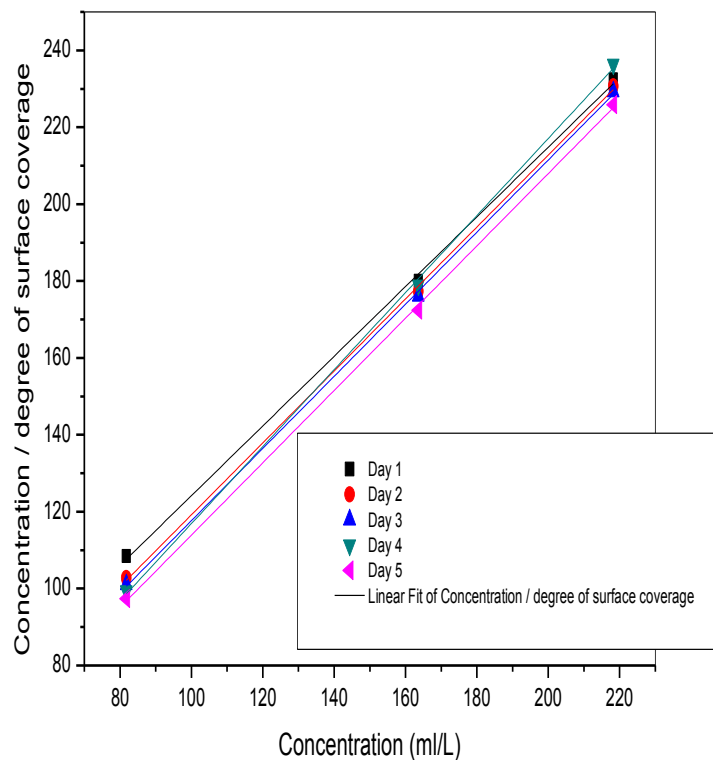
Where  $K$  is the adsorption equilibrium constant,  $\theta$  is the degree of surface coverage. From the results of analysis plots of  $C/\theta$  against concentration shown in Figures 4.11 – 4.12 below is a straight line graph, the slopes of the graphs are close to unity and values of linear correlation coefficient as shown Table 4.11 below are all above 0.95 indicating that the adsorption of the ethanol extracts of *Chrysophyllum albidum* and the Synthetic Inhibitor on mild steel surface in the simulated drilling fluid at different immersion periods properly fits Langmuir adsorption isotherm. Tables 4.11 – 4.12 below shows values of inhibition efficiency, degree of surface coverage ( $\theta$ ),  $C/\theta$  for the Langmuir adsorption isotherm on the adsorption of CA and SI on mild steel while Table 4.13 shows values of the slopes and linear correlation coefficient,  $R^2$  obtained from the graph of  $C/\theta$  against  $\theta$ .

**Table 4.11: Inhibition efficiency, degree of surface coverage of mild steel at different concentration of CA over different periods of immersion.**

<b>Periods of Immersion</b>	<b>Concentration ml/L</b>	<b>Inhibition Efficiency</b>	<b>Surface Coverage(<math>\theta</math>)</b>	<b><math>C/\theta</math></b>	<b><math>\log \theta</math></b>	<b><math>\log C</math></b>
<b>One</b>	81.8	75.4	0.754	108.4	-0.1226	1.9128
<b>Day</b>	163.6	90.9	0.909	180.0	-0.04144	2.2138
	218.2	93.88	0.939	232.4	-0.02734	2.3389
<b>Two</b>	81.8	79.6	0.796	102.76	-0.09907	1.9128
<b>Days</b>	163.6	92.3	0.923	177.24	-0.03480	2.2138
	218.2	94.6	0.946	230.66	-0.0241	2.3389
<b>Three</b>	81.8	80.9	0.809	101.11	-0.09205	1.9128
<b>Days</b>	163.6	92.9	0.929	176.10	-0.0320	2.2138
	218.2	95.15	0.9515	229.32	-0.02159	2.3389
<b>Four</b>	81.8	82.33	0.8233	99.36	-0.08444	1.9128
<b>Days</b>	163.6	91.46	0.9146	178.88	-0.03877	2.2138
	218.2	92.32	0.9232	236.35	-0.0347	2.3389
<b>Five</b>	81.8	84.04	0.8404	97.33	-0.0755	1.9128
<b>Days</b>	163.6	94.90	0.9490	172.39	-0.02273	2.2138
	218.2	96.6	0.9660	225.88	-0.01502	2.3389

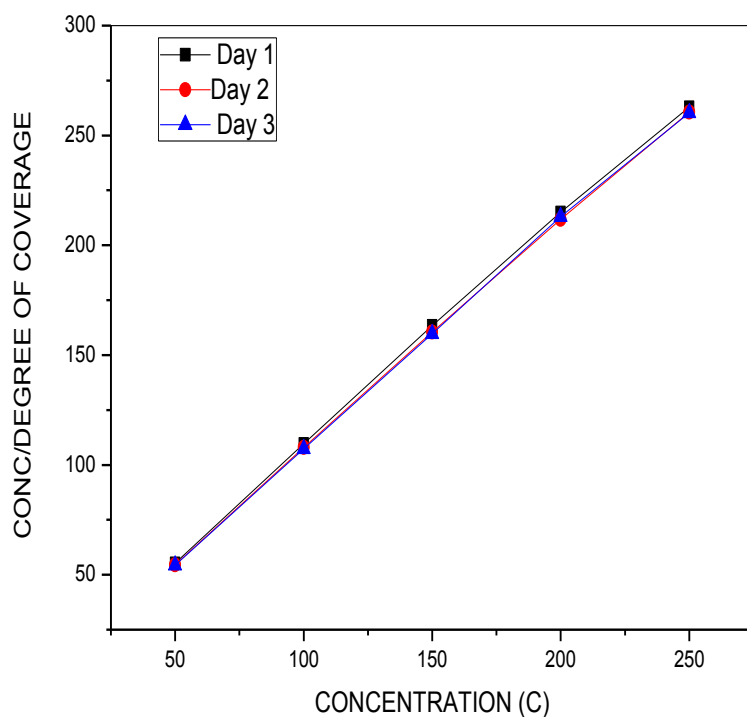
**Table 4.12. Inhibition efficiency, degree of surface coverage of mild steel at different concentration of SI over different periods of immersion.**

<b>Periods of Immersion</b>	<b>Concentration</b>	<b>Inhibition Efficiency</b>	<b>Surface Coverage(<math>\theta</math>)</b>	<b>C/<math>\theta</math></b>	<b>Log C</b>
<b>One Day</b>	50	90.47	0.9047	55.267	1.6989
	100	91.23	0.9123	109.613	2.000
	150	91.94	0.9194	163.50	2.1760
	200	93.02	0.9302	215.08	2.3010
	250	95.13	0.9513	262.98	2.3979
<b>Two Days</b>	50	91.49	0.9149	54.5	1.6989
	100	92.58	0.9258	108.015	2.000
	150	93.50	0.9350	160.42	2.1760
	200	94.40	0.9440	211.86	2.3010
	250	95.93	0.9593	260.607	2.3979
<b>Three Days</b>	50	92.11	0.9211	54.283	1.6989
	100	93.2	0.932	107.296	2.000
	150	93.88	0.9388	159.778	2.1760
	200	93.9	0.939	212.993	2.3010
	250	96.05	0.9605	260.28	2.3979



**Figure 4.11. Langmuir adsorption isotherm of mild steel corrosion in the Simulated Drilling Fluid in the presence of different concentration of the ethanol extract *chrysophyllumalbidum* after one, two, three, four and five days.**

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



**Figure 4.12: Langmuir adsorption isotherm of mild steel corrosion in the Simulated Drilling Fluid in the presence of different concentration of the Synthetic Inhibitor after one, two and three days.**

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

Table 4.13 shows the  $R^2$  values and slopes of the graph of Langmuir adsorption isotherm of the corrosion inhibition of mild steel in the Simulated Drilling Fluid with ethanol extract of CA at different immersion time, while Table 4.14 shows the  $R^2$  values and slopes of the graph of Langmuir adsorption isotherm of the corrosion inhibition of mild steel in the Simulated Drilling Fluid with ethanol extract of CA at different immersion time.

**Table 4.13.  $R^2$  values and slopes of the graph of Langmuir adsorption isotherm of the corrosion inhibition of mild steel in the Simulated Drilling Fluid with ethanol extract of CA at different immersion time.**

<b>Period of Immersion</b>	<b>CA in Simulated Drilling Fluid</b>		
	Slope	$R^2$ values	K
<b>One day</b>	0.90643	0.9987	1.103
<b>Two days</b>	0.93555	0.99921	1.069
<b>Three days</b>	0.938	0.99943	1.066
<b>Four days</b>	1.00179	0.99904	0.998
<b>Five days</b>	0.94049	0.99935	1.063

**Table 4.14.  $R^2$  values and slopes of the graph of Langmuir adsorption isotherm of the corrosion inhibition of mild steel in the Simulated Drilling Fluid with different concentrations of the SI at different immersion time.**

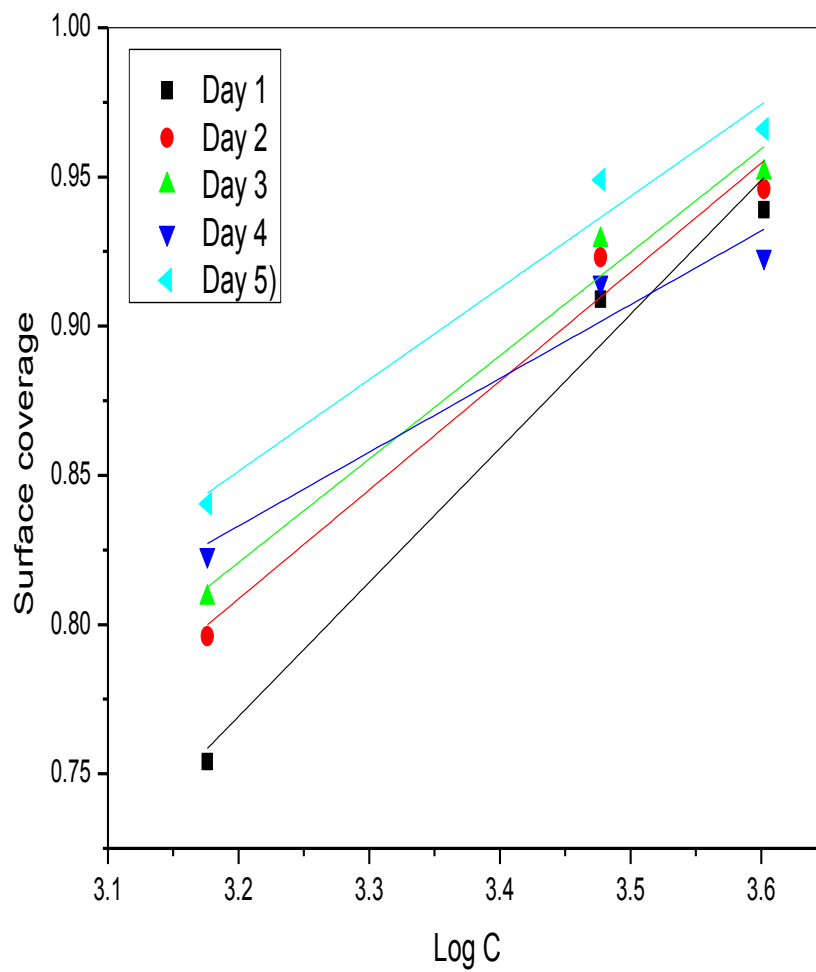
<b>Period of Immersion</b>	<b>SI in Simulated Drilling Fluid</b>		
	Slope	$R^2$ values	K
<b>One day</b>	1.04179	0.99914	1.0699
<b>Two days</b>	1.03212	0.99959	1.0621
<b>Three days</b>	1.03538	0.9994	1.0661

#### 4.8 Temkin adsorption isotherm

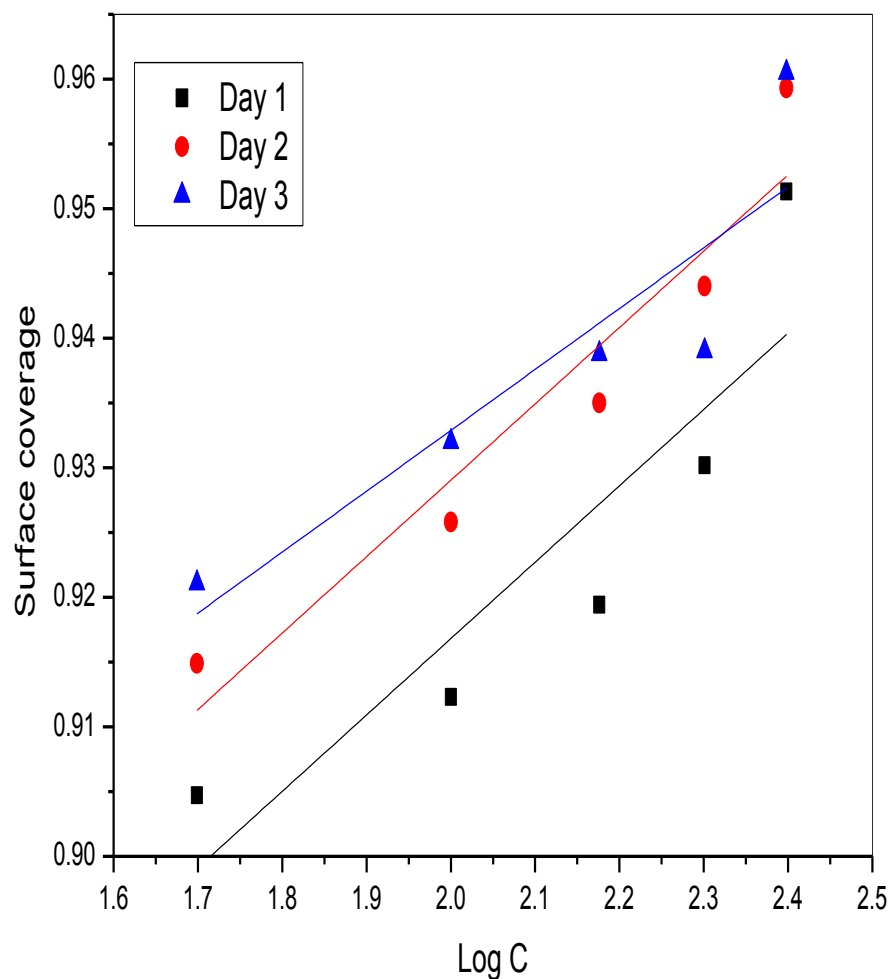
This isotherm takes into accounts of indirect adsorbate-adsorbent interactions on adsorption isotherms. Temkin noted experimentally that heat of adsorption would more often decrease than increase with increasing coverage. The Temkin isotherm model assumes that the adsorption heat of all molecules decreases linearly with the increase in coverage of the adsorbent surface, and that adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy. The Temkin isotherm can be described by Equation (Ayssar *et al.*, 2010; El.Etre, 2003):

$$\Theta = \frac{-2303 \log K}{2a} - \frac{2303 \log C}{2a} \quad (4.4)$$

Where  $a$  is the Temkin interaction parameter,  $\theta$  is the degree of surface coverage of the inhibitor.  $K$  is the equilibrium constant of adsorption and  $C$  is the concentration of the inhibitor. The applicability of the isotherm model to describe the adsorption process was judged based on the correlation coefficients (or values of linear regression)  $R^2$ , which is a measure of goodness of fit (Thilagavathy & Saratha, 2015).



**Figure 4.13: Temkin adsorption isotherm plot of mild steel corrosion in the Simulated Drilling Fluid in the presence of different concentration of the ethanol extract *Chrysophyllum albidum* after one, two, three, four and five days.**



**Figure 4.14: Temkin adsorption isotherm plot of mild steel corrosion in the Simulated Drilling Fluid in the presence of different concentration of the Synthetic Inhibitor after one, two and three days.**

The plots of  $\theta$  against  $\text{Log } C$  shown in Fig. 4.13 above indicated a straight line with high values of correlation coefficient ( $R^2$ ) ( $\geq 0.95$ ) suggesting that the adsorption of components of *Chrysophyllum albidum* (CA) in the simulated drilling fluid on the mild steel follows the Temkin adsorption isotherm. The values of “a” depend on the intermolecular interaction in the adsorption layer and on the heterogeneity of the surface. The high and positive values of “a” (in Table 4.15 below) show the attractive force and a high degree of surface coverage providing better inhibitive property of the extract. The values of K (Table 4.15) denote the strength

between adsorbate and adsorbent. Larger values of  $k$  obtained imply that adsorption is more efficient (Satapathy *et al.*, 2009).

The plots of  $\theta$  against  $\log C$  shown in Fig. 4.14 above indicated a non linear graph with low values of correlation coefficient ( $<0.95$ ) suggesting that the Temkin adsorption isotherm was inadequate in describing the adsorption of the different concentration of the Synthetic Inhibitor (SI) in the simulated drilling fluid on the mild steel surface. The values of  $R^2$ ,  $a$  and  $K$  are shown in Table 4.16 below.

**Table 4.15: Temkin adsorption isotherm parameters and  $R^2$  values of the corrosion inhibition of mild steel in the Simulated Drilling Fluid with ethanol extract of CA at different immersion time.**

Period of Immersion	CA in Simulated Drilling Fluid		
	A	Log K	$R^2$
One day	2.564	1.49	0.9623
Two days	3.155	0.984	0.9573
Three days	3.325	1.21	0.9599
Four days	4.659	0.17	0.9117
Five days	3.75	0.426	0.9500

**Table 4.16: Temkin adsorption isotherm parameters and  $R^2$  values of the corrosion inhibition of mild steel in the Simulated Drilling Fluid with different concentrations of SI at different immersion time.**

Period of Immersion	SI in Simulated Drilling Fluid		
	A	Log K	$R^2$
One day	19.0	13.18	0.7427
Two days	19.0	13.38	0.8881
Three days	24.5	17.85	0.7493

#### 4.9 Effect of Temperature

Temperature studies was carried out on the corrosion inhibition of mild steel in the simulated drilling fluid in the presence of aqueous extracts of CA and SI within temperature ranges of 313K -333K to investigate temperature effect on the corrosion rate and inhibition performance in order to determine the possible mechanism of the adsorption process.

Table 4.14 shows the results of the effect of temperature on the corrosion rate and inhibition performance of mild steel corrosion with and without ethanol extract of CA at 313K to 333K after three hours.

**Table 4.17: Results showing effect of temperature on the corrosion rate and inhibition performance of mild steel corrosion with and without ethanol extract of CA at 313K to 333K after three hours.**

System ml/L	313		323		333	
	Average Corrosion Rate (g/cm <sup>2</sup> hr)	Inhibition Efficiency	Average Corrosion Rate (g/cm <sup>2</sup> hr)	Inhibition Efficiency	Average Corrosion Rate (g/cm <sup>2</sup> hr)	Inhibition Efficiency
<b>Blank</b>	62.60	-	176.52	-	221.70	-
<b>81.8ml/L</b>	3.17	81.91	12.26	86.14	13.45	87.54
<b>218.2ml/L</b>	1.24	92.96	4.01	95.98	5.92	96.45

Result from temperature studies carried out (Table 4.17) within the temperature range of 313K-333K reveals an increase in corrosion rate with rise in temperature of the mild steel in the presence and absence of the ethanol extracts of CA. Highest corrosion rate was recorded at 333K in the absence of the CA.

Also, the result reveals an increase in inhibition efficiency of the ethanol extracts of CA in the simulated drilling fluid with rise in temperature from 313 K to 333K.

The effect of temperature on the corrosion rate and inhibition performance of mild steel corrosion with and without SI at 313K to 333K after three hours is summarized in Table 4.18

**Table 4.18: Results showing effect of temperature on the corrosion rate and inhibition performance of mild steel corrosion with and without SI at 313K to 333K after three hours.**

System ml/L	313		323		333	
	Average Corrosion Rate (g/cm <sup>2</sup> hr)	Inhibition Efficiency	Average Corrosion Rate (g/cm <sup>2</sup> hr)	Inhibition Efficiency	Average Corrosion Rate (g/cm <sup>2</sup> hr)	Inhibition Efficiency
<b>Blank</b>	62.60	-	176.52	-	221.70	-
<b>50ml/L</b>	3.17	80.96	11.96	86.24	12.16	87.15
<b>250ml/L</b>	1.20	93.49	43.09	96.54	4.72	97.35

The result from temperature studies carried out within the temperature range of 313K-333K as shown in Table 4.18 reveals an increase in corrosion rate with rise in temperature of the mild steel in the presence and absence of the synthetic inhibitor. Highest corrosion rate was recorded at 333K in the absence of SI. Again, the result reveals an increase in inhibition efficiency of the synthetic inhibitor in the simulated drilling fluid with rise in temperature from 313 K to 333K.

#### **4.10 Discussion of Results from Temperature Studies**

Temperature studies carried out within the temperature range of **313K – 333K** is summarized in table 4.17 and 4.18 above. The results obtained reveal an increase in corrosion rate with rise in temperature of the test specimen in the test media in the presence

and absence of CA and SI. Highest corrosion rate was recorded at 333K in the absence of both inhibitors. The effect is expected because as the temperature increases the rate of corrosion of mild steel increases due to increase in the average kinetic energy of the reacting molecules. It can also be seen from table 4.17 that the corrosion rate decreased in the presence of both inhibitors as compared to their absence which is due to the mitigating effect of the inhibitors on the corrosion rate of the mild steel.

From the data it can be inferred that the protective layer of the organic complex compound formed on the mild steel surface was more stable as the temperature increased from 313K to 333K.

Similar results were obtained from (Phillip et al., 2002; Vasudha et al., 2013;). However it was observed that inhibition efficiency of the test specimen decreased progressively with rise in temperature in the simulated drilling fluid in the presence of both CA and SI. This might be attributed to the desorption of the inhibitors on the mild steel surface as the temperature rises from 313K to 333K.

#### **4.11 Thermodynamic Studies.**

Temperature studies give an insight on the possible mechanism of the inhibition process, the variation of inhibition efficiency with temperature (Tables 4.17 & 4.18 above) and the apparent activation energies of the inhibition process. Table 4.19 helps to predict the mechanism of the adsorption process. In general two types of adsorption mechanism can be used to describe the adsorption of an organic species on a corroding metal specimen namely: physical adsorption or physisorption and chemical or chemisorption. In the former the inhibiting molecules are physically attached to the metal species via weak Van der Waals forces of attraction (Popova et al., 2003). The physisorbed molecules are attached at the

cathodic site, retarding metal dissolution by reducing rate of cathodic reaction. In chemisorption or chemical adsorption the inhibiting molecules are attached to the corroding metal species via strong chemical bonds, the chemisorbed molecules are attached at the anodic site thus inhibiting the dissolution of the metal species. It has been suggested that the most efficient inhibitor is one which inhibits the anodic site by chemisorption (Popova *et al.*, 2003).

### **Activation Energy $E_a$ .**

The activation energy of the process was calculated from the Arrhenius equation stated in equation (3.4) above. Results of the activation energies of the adsorption process of both inhibitors in the test media are given in the Table 4.19 below.

**Table 4.19: Ea values of the corrosion inhibition of mild Steel in the simulated drilling fluid in the presence of ethanol extract of CA and the synthetic inhibitor SI at temperature ranges of 313K - 333 K**

<b>System</b>	<b>Ea of Specimen in simulated drilling fluid in the presence of CA</b>	<b>System</b>	<b>Ea of Specimen in simulated drilling fluid in the presence of SI</b>
<b>Blank</b>	52.107kJm <sup>-1</sup>	<b>Blank</b>	52.107kJm <sup>-1</sup>
<b>81.8ml/L</b>	62.91 kJm <sup>-1</sup>	<b>50ml/L</b>	58.25kJm <sup>-1</sup>
<b>218.2ml/L</b>	67.73kJm <sup>-1</sup>	<b>250ml/L</b>	59.34kJm <sup>-1</sup>

Results obtained (in Table 4. 19 above) revealed that activation energy values in the presence of ethanol extract of CA and SI concentration at 81.8ml/L and 50 ml/L in the simulated drilling fluid respectively were higher than in the blank solution (i.e in the absence of the extracts) whereas activation energy values of the adsorption process in the simulated drilling fluid were lower at 218.2 ml/L of CA and 250 ml/L of SI than in their absence. It has been suggested that a decrease in inhibition efficiency with rise in temperature followed by analogous increase in corrosion activation energy in the presence of the inhibitor compared to its absence can be attributed to physical adsorption of the organic molecules on the metal surface, on the other hand an increase in inhibition efficiency with rise in temperature followed by a corresponding decrease in corrosion activation energy in the presence of the inhibitor than in the absence suggests chemisorption of the inhibiting molecules on the

corroding metal (Oguzie *et al.*, 2010). Hence the results obtained from this study suggests chemisorption of the inhibiting species in the simulated drilling fluid at 81.8ml/L and 218.2 ml/L concentrations of CA and 50 ml/L and 250 ml/L concentrations of SI respectively. Similar results have been reported by Popova *et al.*, 2003; Thilagavathy and Saratha, 2015.

### **Gibb's Free Energy**

Gibb's free energies of the reaction was calculated using the relationship between the equilibrium constant of water extract of CA and the concentrations of SI expressed mathematically in equation (3.5) above. Results obtained are given in the Table 4.20 below.

**Table 4.20:  $\Delta G$  values of the corrosion of mild steel in the simulated drilling fluid in the presence of ethanol extract of CA and SI at temperature ranges of 313K -333K**

Temperature in K	$\Delta G$ of CA in simulated drilling fluid	$\Delta G$ of SI in simulated drilling fluid
313	-20.763 KJm <sup>-1</sup>	-22.321 KJm <sup>-1</sup>
323	-21.959KJm <sup>-1</sup>	-23.997 KJm <sup>-1</sup>
333	-22.973KJm <sup>-1</sup>	-24.661 KJm <sup>-1</sup>

The negative values of  $\Delta G$  (Table 4.20) ensure spontaneity of the adsorption process and stability of the adsorbed layer on the mild steel surface. In general  $\Delta G$  values of -20 KJm<sup>-1</sup> or lower are consistent with physisorption while those around -40KJm<sup>-1</sup> or higher involves charge sharing transfer from organic molecules to the metal surface to form co – ordinate type of bond indicating chemisorptions(Umoren *et al.*, 2009; Tao *et al.*,2010). Results obtained shows that  $\Delta G$  values are negative in all cases indicating spontaneity. It also has values above -20 KJm<sup>-1</sup>, which is consistent with literature. Thus authenticates the involvement of chemical adsorption and agrees with the works of (Liang *et al.*,2011). This implies that the plant extracts CA and synthetic inhibitor SI adheres on the corroding metal and gives a very strong inhibition.

## Heat of Adsorption $Q_{ads}$

The energy of adsorption which is approximately equal to enthalpy change or change in heat content of reaction  $\Delta H_{ads}$  was obtained using the trend of change in degree of surface coverage with temperature stated mathematically in equation (3.7) above. The Table 4.21 below shows the values of  $\Delta H_{ads}$  of the adsorption process:

**Table 4.21:  $\Delta H_{ads}$  values of the corrosion of mild steel in simulated drilling fluid in the presence of ethanol extracts of CA and SI at 313K – 333K**

<b>System</b>	<b><math>\Delta H_{ads}</math> values of CA in the simulated drilling fluid</b>	<b>System</b>	<b><math>\Delta H_{ads}</math> values of SI in the simulated drilling fluid</b>
<b>81.8ml/L</b>	<b>16.16 <math>\text{KJm}^{-1}</math></b>	<b>50ml/L</b>	<b>17.04 <math>\text{KJm}^{-1}</math></b>
<b>218.2 ml/L</b>	<b>29.67 <math>\text{KJm}^{-1}</math></b>	<b>250ml/L</b>	<b>10.15 <math>\text{KJm}^{-1}</math></b>

Results obtained as shown in Table 4.21 above reveal that  $\Delta H_{ads}$  of the adsorption process is positive in the simulated drilling fluid in both inhibitors under study. In general negative value of  $\Delta H_{ads}$  reflects exothermic reaction which implies that inhibition efficiency decreases with rise in temperature, on the other hand, positive  $\Delta H_{ads}$  values is an indication of an endothermic reaction reflecting that inhibition efficiency increases with rise in temperature (Atkins, 1998). Thus results from the study indicates an endothermic reaction occurring in the adsorption of both extract in the acid medium also  $\Delta H_{ads}$  values were less

than  $80 \text{ KJm}^{-1}$  in all cases which is an indication that physisorption is involved in the adsorption mechanism.

#### **4.12. Proposed Mechanism of Inhibition**

The mechanism of inhibition can be explained based on the mode of adsorption of inhibiting species (i.e whether molecular or ionic), factors such as composition and structure of the inhibitor, the nature of the metal surface, type of acid anion and chemical changes to the extract contributes to the mechanism of inhibition. In addition, structural and electronic parameters such as functional group, steric and electronic effect may be responsible for inhibition efficiency of any inhibitor. The presence of the phytoconstituents such as tannins, saponins, terpenoids, flavonoids e.t.c. have been proven from literature to be the major constituents present causing inhibition. These phyto-constituents contain lone pair of electrons present on a hetero-atom (i.e oxygen, phosphorous, sulphur and nitrogen), pi-bond, triple bond(e.g cyano group) in their functional group which are characteristics of a good corrosion inhibitor. They act by blocking the active corrosion sites on the metal surface, thus the adsorption process involves bonding of the free electrons of the inhibitor with the metal. Consequently inhibiting characteristics of the extract can be attributed to the presence of these phyto-constituents, the main constituent causing inhibition is beyond the scope of this work because results of analysis does not include isolation of these compounds. Corrosion inhibitors from plant origin are complex in nature therefore it is difficult to isolate the particular constituents that effect inhibition (Oguzie *et al.*, 2007; Vasant & Bansal, 2013). The adsorption mechanism can also be considered from the electrostatic force of attraction existing between inhibiting organic ions and the electrically charged metal surface at the metal/solution interphase. Temperature studies reveal that the inhibition performance of both plant extracts CA and synthetic inhibitor are higher in the simulated drilling fluid

media at higher temperature. This can be attributed to the chemical bonding between the ions of the inhibitors and the charged metal surface. A corroding metal specie possesses a positive charge in  $\text{H}_2\text{SO}_4$  media and such protonated species are poorly adsorbed at the metal/solution interphase (Oguzie, 2006). Results of the energy of activation values indicates that the adsorption process occurred by chemisorptions hence, it can be deduced that the mechanism of the adsorption is mainly by chemisorptions.

## CHAPTER FIVE

### CONCLUSION AND RECOMMENDATIONS

#### 5.1 CONCLUSION

*Chrysophyllum albidum* CA, is as good a corrosion inhibitor as the Synthetic Inhibitor SI, in inhibition of mild steel in the simulated drilling fluid used. Gravimetric result reveals highest inhibition efficiency 96.60% and 96.05% in the simulated drilling fluid at 218.2ml/L and 250 ml/L of CA and SI respectively.

Potentiodynamic polarization results shows that the inhibitors are of mixed type, that is both anodic and cathodic reactions are inhibited in the presence of ethanol extract of *Chrysophyllum albidum* CA and synthetic inhibitor SI.

The adsorption isotherm models successfully applied shows that the adsorption of ethanol extract of CA on the surface of the mild steel obeys the Langmuir and Temkin adsorption isotherms while the adsorption of SI on the surface of the mild steel obeys only the Langmuir isotherm.

Temperature studies reveal highest inhibition efficiency of 96.45% and 97.35% in at 333 K for CA and SI respectively indicating a small difference in inhibition between CA extract and SI. This clearly shows that the ethanol extracts of CA can act as suitable substitute for the SI in drilling fluid production. Temperature studies which gives an insight to the possible mechanism of the adsorption process suggests chemisorptions of the inhibiting species at 81.8ml/L and 218.2ml/L of CA and 50mg/L and 250mg/L of SI in the simulated drilling fluid. The activation energy values were found to be 64.26 KJm<sup>-1</sup> and 54.50 KJm<sup>-1</sup> in presence of CA and 56.22 KJm<sup>-1</sup> in its absence, and 60.14KJm<sup>-1</sup> and 53.64 KJm<sup>-1</sup> in the presence of SI and 56.22 in its absence. In addition, change in Gibb's free

energy  $\Delta G$ , reveals negative values in all cases indicating spontaneity of the process. The heat of adsorption  $Q_{ads}$  which is approximately equal to  $AH_{ads}$  was negative in all concentrations of CA and SI in 1M  $H_2SO_4$  which implies an endothermic reaction occurring in both *Chrysophyllum albidum* CA and synthetic inhibitor SI.

Finally, the above results obtained indicates that *Chrysophyllum albidum* CA, extract can be used as an alternative to the synthetic inhibitor in inhibition of mild steel in drilling fluid or acidic environment.

## 5.2. Recommendations

Other plant extracts should be similarly investigated for their inhibition strength or efficiency for drill mud application.

The study did not extend on the use of electron impedance spectroscopy (EIS) in the study of the corrosion inhibition behavior of the *Chrysophyllum albidum* CA, extracts. It is recommended for further study on this work in order to compare and examine parameters determined from such study and that of the system in the present study.

Further studies can be carried out on the CA extract such as GC-Mass Spectrometry to determine the exact component in the CA extract responsible for the inhibition.

## 5.3 Contribution to Knowledge

The study has revealed that at 218.2ml/L *Chrysophyllum albidum* CA, is as good as the synthetic inhibitor SI. Hence CA extract can be used as an alternative source of corrosion inhibition at that concentration or at higher concentration in drilling fluids, since the inhibition efficiency of CA increased with increase in its extract concentration.

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