COMPARATIVE STUDIES ON THE CORROSION INHIBITION OF TIN IN ACIDIC AND ALKALINE MEDIA USING HENNA LEAVES POWDER AND CAFFEINE AS INHIBITORS

BY

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A DISSERTATION SUBMITTED TO THE DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY, FACULTY OF SCIENCE, BAYERO UNIVERSITY KANO, IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE (M.Sc.) IN PHYSICAL CHEMISTRY

MARCH, 2017

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DECLARATION

I hereby declare that this research work titled "Comparative Studies on the Corrosion Inhibition of Tin in Acidic and Alkaline Media using Henna Leaves Powder and Caffeine as Inhibitors" is the product of my research efforts, undertaken under the supervision of Prof. Muhammad Bashir Ibrahim and has not been presented anywhere for the award of a degree or certificate. All sources of information have been duly acknowledged.

……………………. ……………………

Zakariyau Sulaiman Date

(SPS/13/MCH/00080)

CERTIFICATION

This is to certify that the research work for this Dissertation and its subsequent preparation by Zakariyau Sulaiman (SPS/ 13/ MCH/ 00080) were carried out under my supervision.

…………………………………… …………………..

Prof. Muhammad Bashir Ibrahim Date

(Supervisor)

APPROVAL

This dissertation has been examined and approved for the award of Masters in Physical Chemistry.

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ACKNOWLEDGEMENT

My profound gratitude goes to The Almighty Allah Subhanahu Wata ala (S W T) for guiding and giving me the strength to carry out the work successfully.

My sincere appreciation goes to my able and kind supervisor Prof. M. B. Ibrahim and my internal examiner Dr. Umar Ibrahim Gaya for their tireless efforts day and night to see that this work come to an end successfully. May Allah reward them abundantly and forgive them for their wrong deeds (Ameen).

My gratitude goes to my able post graduate co-ordinator Dr. Umar Sani, Head of department Dr. Haruna Musa, Dr. Ayuba Muhammad Abdullahi, Professor A.A Audu, Professor S. Y. Mudi, Dr. Kabiru Abdu and the entire lecturers of the Department.

I will like to acknowledge my guardians, brothers and sisters for their moral support and encouragement throughout my stay in the University among whom are Dr. Sulaiman Abdulkareem, his wife Haj. Aisha Ismaila, Muhammad Sani, Rukkayya Sulaiman, Fatimat Sulaiman and others. May Allah shower his blessings on them all (Ameen).

I will like to acknowledge those that showed love and care to me among whom are friends Buhari Alfa Sulaiman, Mustapha Omenesa Idris, Yusif Ahmed Jibril, Bashir Abdulkareem Rogo, Ibrahim Abdulkareem and others. May Allah (S W T) continue to guide and guard us in all our academic pursuits (Ameen).

DEDICATION

This report is dedicated to my lovely parents, late Mallam Sulaiman Muhammad and Mallama Khadijat Sulaiman Muhammad. May The Almighty Allah shower his blessings and mercy on them and grant them Jannatul Firdausi (Ameen).

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ABSTRACT

The corrosion behaviour of Tin at various period of immersion, corrodent concentration, and the inhibition properties of *Lawsonia inermis L* powder *and* Caffeine in HCl and NaOH solutions using weight loss technique was investigated at temperatures ranged 25-50 ^{0}C and at optimum inhibitor concentration (0.5%) in which the overall results obtained showed that both inhibitors have good performance and could be used to prevent the corrosion of the metal in the tested media. Among which leaves extract of *Lawsonia inermis* is the most effective in alkaline solution. Inhibition efficiency of *Lawsonia inermis L* was found to be 93.10% at 50 ^{0}C and 95.45% at 30 ^{0}C in the alkaline solution while caffeine showed a minimum efficiency in alkaline solution of 44.83% at 50 ^{0}C and 54.55% at 30 ^{0}C. This revealed that the inhibition efficiency decreased with increased in temperature but increased with increasing inhibitor concentrations. The adsorption was found to obey Freundlich (0.997 R^2), Frumkin (0.990 R^2) and Temkin (0.988 R^2) isotherm. Physical adsorption mechanism is proposed from the trend of ΔG_{ads} (-3.280 to -1.047 kjmol^{-1}) obtained. The negative values of ΔG_{ads} (-3.280 to -1.047 kjmol^{-1}) show the spontaneity of the inhibition process. The increase in the activation energy (Ea= 19.075 to 29.589 kjmol^{-1}) of the inhibited solutions above that of the blank (Ea= 9.405 kjmol^{-1} acid and 10.562 kjmol^{-1} alkaline) and hence the inhibition process with values less than the threshold value of 80kJ/mol support the mechanism of physical adsorption process. FTIR spectroscopy was used to confirm the presence of both inhibitors in the tested media.

CHAPTER ONE

1.0 INTRODUCTION

1.1 BACKGROUND TO THE STUDY

Corrosion is the deterioration of materials by chemical interaction with their environment (Ajayi, 2003). The term corrosion is sometimes applied to the degradation of plastics, concrete and wood, but generally refers to metals. It may also be defined as surface damage of metals in an aggressive environment (salt, acid and alkaline) (Lahodny-Sarc, 1994). Corrosion has been described by IUPAC as an electrochemical process in which electrons between metal surface and aqueous electrolytic solution are rearranged; this gives rise to destructive disintegration of metal surface as a result of the electrochemical reaction (Winston and Herbert, 2008). The basic process of metallic corrosion in aqueous solution consists of the anodic dissolution of metal and the cathodic reduction of oxidants present in the solution; (Sharma, 2012).

$M_m \rightarrow M^{2+}_{(aq)} + 2e^-_m$ Anodic Oxidation

$2Ox_{aq} + 2e^-_m \rightarrow 2Red\,(e^-_{redox})_{aq}$ Cathodic Reduction

In the formular, M_m is the metal in the state of metallic bonding, $M^{2+}_{(aq)}$ is the hydrated metal ion in aqueous solution, e^-_m is the electron in the metal, $Ox_{(aq)}$ is an oxidant, $Red\,(e^-_{redox})_{aq}$ is a reductant ,and e^-_{redox} electron in the reductant. The overall corrosion reaction is then written as follows (Sharma*,* 2012):

$$M_m + 2Ox_{aq} \rightarrow M^{2+}_{aq} + 2Red\,(e^-_{redox})_{aq}$$

A typical example of this is the attack on tin by hydrochloric acid. When tin is placing in hydrochloric acid it dissolves forming tin chloride with the release of hydrogen gas (Quraishi *et al.*, 2004). Similarly, NaOH solution attacks tin forming sodium stannate (a colourless complex salt and octahedral in shape) with the release of hydrogen gas. During metallic corrosion, the rate of oxidation equals to the rate of reduction in terms of electron production and consumption.

Acidic Media

$$Sn_{(s)} \rightarrow Sn^{2+}_{(aq)} + 2e^- \qquad (1)$$

$$2Cl^-_{(aq)} + 2H^+_{(aq)} + 2e^- \rightarrow 2Cl^-_{(aq)} + H_{2(g)} \qquad (2)$$

$$Sn_{(s)} + 2HCl_{(aq)} \rightarrow SnCl_{2(s)} + H_{2(g)} \qquad (3)$$

Basic Media

Anodic Half Cell Reaction:

$$Sn_{(s)} \rightarrow Sn^{4+}_{(aq)} + 4e^- \qquad (4)$$

Cathodic Half Cell Reaction:

$$4H_2O_{(aq)} + 4e^- \rightarrow 4OH^-_{(aq)} + 2H_{2(g)} \qquad (5)$$

$$Sn_{(s)} + 4H_2O_{(l)} \rightarrow Sn^{4+}_{(aq)} + 4OH^-_{(aq)} + 2H_{2(g)} \qquad (6)$$

At the Tin Surface

$$Sn^{4+}_{(aq)} + 2Na^+{}_{(aq)} + 2OH^-{}_{(aq)} + 4OH^-{}_{(aq)} \rightarrow Na_2[Sn(OH)_6]_{(s)} \qquad (7)$$

Overall Reaction:

$$\Rightarrow Sn_{(s)} + 2NaOH_{(aq)} + 4H_2O_{(l)} \rightarrow Na_2[Sn(OH)_6]_{(s)} + 2H_{2(g)} \qquad (8)$$

1.1.1 Research Justification

Corrosion of tin has been a subject of research interest due to their high technological value and wide range of industrial applications especially in food and household industries. Tin and its alloys are found useful for many engineering applications because of their lightness and strength, thermal and electrical conductivity, heat and light reflectivity and hygienic and non-toxic qualities. Tin is a reactive metal according to the electrochemical series ($E_{0} = -0.14V$), but it is non-reactive in moisture due to the formation of a stable oxide film on its surface. Tin is not attacked by pure water but dissolves in aqueous acids with the liberation of hydrogen gas. Acids like hydrochloric acid, sulphuric acid are used for drilling operation, pickling and descaling. Many workers have studied corrosion of tin in HNO_3 solution for which the mechanism was proposed as follows (Kumpawat *et al.*, 2012).

$$\mathrm{Sn_{(s)}} \rightarrow \mathrm{Sn^{2+}_{(aq)}} + 2e^{-} \qquad (9)$$

$$\mathrm{2NO_3^-{}_{(aq)}} + \mathrm{2H^+_{(aq)}} + 2e^{-} \rightarrow \mathrm{2NO_3^-{}_{(aq)}} + \mathrm{H_{2(g)}} \qquad (10)$$

$$\mathrm{Sn_{(s)}} + \mathrm{2HNO_3^-{}_{(aq)}} \rightarrow \mathrm{Sn(NO_3\,)_{2(s)}} + \mathrm{H_{2(g)}} \qquad (11)$$

In order to reduce the corrosion of metals, several techniques have been applied which basically comprises those protective measures providing separation of metal surfaces from corrosive environments or those which cater for adjustment or altering the environment. These various methods of corrosion prevention include cathodic protection, anodic protection, coating and the use of corrosion inhibitor. Most commonly, corrosion inhibitors are classified as anodic, cathodic or mixed according to their influence on the electrochemical reaction involving metal, and their environment. Corrosion inhibitors have been in use for several decades and the most familiar examples of their applications are in paints and coatings on metals where nitrate, chromate, phosphate, benzoates, borates and oxides are incorporated, Nitrite is being used as inhibition admixture in concrete reinforcement (Aramide, 2009). It is well established that inhibitors function in one or more ways to control corrosion: by adsorption of a thin film onto the surface of a corroding material, by inducing the formation of a thick corrosion product, or by changing the characteristics of the environment resulting in reduced aggressiveness (Aramide, 2009). The focus of this work is to arrive at the optimum concentration of the inhibitor concentration to give adequate corrosion protection to tin sheet in acidic and basic environment.

1.1.2 Statement of the Research Problem

The practical method mostly used for protection of metals against corrosion especially in acid solutions to prevent unexpected metal dissolution and acid consumption is the use of inhibitors (Olasehinde *et al.,* 2012). Most corrosion inhibitors protect the corrosion of metals when they are adsorbed on the surface of the metal (Abdallah, 2004a, b). The most effective and efficient inhibitors are the organic compounds containing π bonds, hetero atoms (P, S, N, and O) and inorganic compounds such as chromates and nitrites (Lece *et al.,* 2008). However, the used of these compounds have been questioned lately due to the several negative effects they have caused in the environment (Broussard *et al.*, 1997). As a result, some local plants owing to their natural origin and non-toxic characteristics seem to be ideal alternative to replace the traditional and synthetic organic toxic corrosion inhibitors (Newman and Cragg, 2007). The use of inhibitors is one of the best options of protecting metals and alloys against corrosion (Winston and Herbert, 2008). The environmental toxicity of organic corrosion inhibitors has prompted the search for green corrosion inhibitors as they are biodegradable, do not contain heavy metals or other toxic compounds. In addition to being environmentally friendly and ecologically acceptable, plant products are inexpensive, readily available and renewable. Investigations of corrosion inhibiting abilities of tannins, alkaloids, amino acids, and organic dyes of plant origin are of interest. In recent years, sol-gel coatings doped with inhibitors show real promise (Uzoma *et al*., 2012). Although substantial research has been devoted to corrosion inhibition by plant extracts, reports on the detailed mechanisms of the adsorption process and identification of the active ingredient are still scarce. Development of computational modelling backed by wet experimental results would help to fill this void and help to understand the mechanism of inhibitor action, their adsorption patterns, the inhibitor metal surface interface and aid the development of designer inhibitors with an understanding of the time required for the release of self-healing inhibitors (Rani and Basu, 2012). Metallic corrosion is one of the problems we have often encountered in our industrialized society; hence it has been studied comprehensively since the industrial revolution in the late eighteen century which was found associated with the loss of capital assets and it has also influenced the food industries as well as causing enormous wastage of food substances due to metallic contamination, as a result it to huge economic losses to canning industries.

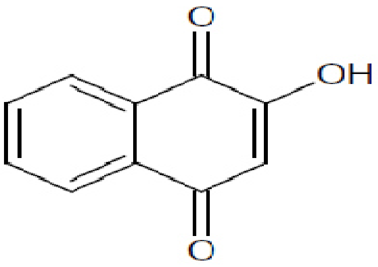
1.1.3 Scope of the Study

The research will be carried out and limited to establish the good fit inhibitor, analysis of; corrosion rate, corrosion product, effect of temperature, inhibition efficiency, inhibiton mechanism, adsorption mechanism, thermodynamic and kinetic parameters on the tin coupons at Bayero University Kano in Gwale Local Government Area Kano State, Nigeria. The data will be generate from both henna and caffeine in both hydrochloric acid and sodium hydroxide solutions. The tin sheet, Caffiene, NaOH and HCl used were all obtained from BDH Company made in England and China.

1.1.4 The Plant Under Study

Lawsonia inermis L, commonly known as “Henna” (called *Lalle* in Hausa language, *Mehndi* in native language of India and Pakistan) is a well branched shrub or small tree frequently cultivated in many tropical and warm temperature regions of Nigeria, Pakistan, India, Egypt, Sudan, Iran, Yemen and Kenya. Large scale cultivation for the sake of leaves which yield dye is confined to India, Egypt, Pakistan and Sudan. Powdered leaves of this plant (aqueous paste) are used as a cosmetic for dyeing hands and hairs. The dyeing properties as well as the UV light absorption, antibacterial, antispasmodic and corrosion inhibition were attributed to the presence of Lawsone, 2-hydroxy-1,4-naphthaquinone having colour index number 75486 (Al-Sehaibani,2000; Dweck,2002). The phenotype of the plant is given in Figure 1.1. The structure of the active compound is as shown in scheme 1.1.

Figure 1.1: Henna plant

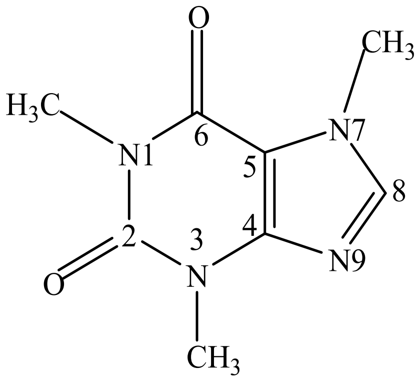


2-Hydroxy-1,4-naphthaquinone

Scheme1.1: Chemical Structure of the Active Compound in Henna

1.1.5 Caffeine

Good results have been obtained using the so called Caffeine (1, 3, 7-trimethylxanthine) as a naturally occurring compound largely found in foods which is not associated with toxicity. The chemical structure of the compound in caffeine is as shown in scheme 1.2 (Fernanado *et al.*, 2014).



Scheme 1.2: Chemical Structure of Caffeine (1, 3, 7-trimethylxanthine)

Environmental-friendly or eco-friendly corrosion inhibitors, which are employed as single compounds, polymers, natural oils or extracts in aqueous solutions, caffeic, L-ascorbic and succinic acids have been recommended by Fernando *et al.* (2014) as potential corrosion inhibitors for mild steel.

1.1.6 Research Hypothesis

Tin is a moderately corrosion resistant material that is widely used in tinplate for food beverage. Tinplate is light gauge, cold reduced, low carbon steel, coated with commercially pure tin. It has the strength, corrosion resistant and lustrous of tin. About one third of the world tin production goes into the manufacture of tinplate. The tin provides sterilization of the foodstuff within the hermetically sealed can, giving long, safe ambient shelf life with minimal use of preservatives. Since tinplate has a vital role for the canned food industry, there is need to develop a method of protecting tin from corrosion damage.

Therefore, the present study shall attempt to explore the possibility of using Henna leaves and Caffeine powder for the inhibition of the corrosion of tin metal in HCl and NaOH solutions and has been designed to evaluate as well as to determine the effective organic substance that could be used as a preventive measure to protect corrosion of tin metal in the acidic and alkaline solutions. The factors that mainly affect internal corrosion of food cans include the properties of tin plate, nature of food process and processing conditions as well (Saguy *et al.*, 1973).

1.1.7 Research Questions

1- Why does corrosion of tin is generally much slower than that of iron and steel in an aggressive media? explain this statement.

2- What is the effect of inhibitor on the corrosion process?

3- Are there optimum conditions of temperature and concentration for corrodent either with or without inhibitor system?

4- What are the consequences of activation energy, gibb's free energy and kinetic of tin metal in the presence and absence of inhibitor?

5- Is there any isotherm model that closely fits the experimental data?

6- How would the thermodynamic properties of the adsorption process relate the experimental data?

1.2 CORROSION MONITORING TECHNIQUES

Corrosion process can be monitored in different ways depending on the information required to be determined such as corrosion product, thermodynamic and kinetic properties of the process which depend on the type of corrosion under study (Hussin and Kasim, 2010). These techniques include the following

1. *Electrochemical methods which involve the use of*
    a. Electrical resistance probes
    b. Electrochemical probes
    c. Potentio-static method
2. *Gravimetric (weight loss coupons) method*
3. *Gasometric or hydrogen evolution method*
4. *Thermometric method*

Gravimetry includes all analytical methods in which the analytical signal is a measurement of mass or a change in mass. When you step on a scale after exercising you are making, in a sense, a gravimetric determination of your mass. Mass is the most fundamental of all analytical measurements, and gravimetry is unquestionably the oldest quantitative analytical technique. The publication in 1540 of Vannoccio Biringuccio's *Pirotechnia* is an early example of applying gravimetry—although not yet known by this name—to the analysis of metals and ores. Although gravimetry no longer is the most important analytical method, it continues to find use in specialized applications (Sulaiman *et al,* 2012).

1.3 AIM AND OBJECTIVES

Aim

The aim of this research work is to investigate the corrosion behaviour of tin sheet in acidic and alkaline solutions as well as to test the effectiveness of henna leaves and caffeine as inhibitors.

Objectives

The objectives include:

i. To study the effect of immersion time on the concentration of corrodents

ii. To find optimum concentration of corrodent at equilibrium time

iii. To study the effect of temperature at optimum concentration

iv. To ascertain the inhibition efficiency at optimum temperature

v. To investigate the adsorption characteristics of the inhibitor

vi. To study the thermodynamic and kinetic properties of the process

1.4 THEORETICAL FRAME WORK

The degree of surface coverage (ϴ), inhibition efficiency (%I.E) of the inhibitor and corrosion rates (CR in mm/y) can be calculated from the average weight loss results using Equations 12, 13 and 14 (Kumpawat *et al*., 2012).

$$\theta = \frac{\Delta w_1 - \Delta w_2}{\Delta w_1} \qquad (12)$$

$$\%1.E = \frac{\Delta w_1 - \Delta w_2}{\Delta w_1} \times 100 \qquad (13)$$

Where ΔW_1 and ΔW_2 are the weight loss of the metal in uninhibited and inhibited solution, respectively.

$$\text{Corrosion rate (mm/y)} = \frac{\Delta w \times 87.6}{A \times t \times d} \qquad (14)$$

Where, ΔW is weight loss in mg, A is area of specimen in cm^2, t is time of exposure in hours, d is the density of metal in g/cm^3 and 87.6 is a conversion factor. Equations (15) and (16) are the integrated rate laws for the first and second order reactions. Also the half-life of first and second order reactions is related to the rate constant according to equation (17) where, wl_t is the weight loss in g at time t, k_1 and k_2 are the rate constant for first and second order, respectively, t is the time of exposure, 2.303 is a constant number for first order, wl_{t_o} is the weight loss in g at time t = 0, $[A]_o$ is the concentration of active specie and $t_{1/2}$ is the half life. Equations (18), (19) and (20) are thermodynamics equations for activation energy, entropy, enthalpy and free energy of corrosion process where, CR is the corrosion rate, A is Arrhenius pre-exponential frequency factor, T is the absolute temperature, R is the universal gas constant, Ea is a quantity characteristic of the adsorption known as activation energy, N is Avogadro's constant, h is Planks constant, $\Delta G_{corr,}$ is free energy of corrosion, ΔH_{corr} is the enthalpy of corrosion and ΔS_{corr} is the entropy of corrosion. Equations (21) and (22) are Gibb's free energy of adsorptions and langmuir isotherm and its dimensionless equilibrium parameters, (23) Temkin isotherm, (24) is Frumkin isotherm, (25) is Flory-Huggins isotherm, (26) is El-Awady isotherm, and (27) is Freundlich isotherm equations (Ituen *et al*., 2013). Where, K_{ads} is the adsorption equilibrium constant, 55.5 is the water concentration, C is the inhibitor concentration, a is the adsorbate interaction parameter and Θ is the surface coverage.

$$-\log(wl)_t = \frac{k_1 t}{2.303} \tag{15}$$

$$\frac{1}{wl_t} = k_2 t + \frac{1}{wl_{t\circ}} \tag{16}$$

$$t_{1/2} = \frac{0.693}{k_1} \tag{17a}$$

$$t_{1/2} = 1/k_2[A]_\circ \text{ or } t_{1/2} = 1/k_2 a \tag{17b}$$

$$CR = A\exp\left(\frac{-Ea}{RT}\right) \tag{18a}$$

$$\text{Log (CR)} = \log A - Ea/(2.303RT) \tag{18b}$$

$$\log\left(\frac{CR}{T}\right) = \log\left(\frac{R}{Nh}\right) + \frac{\Delta S_{corr}}{2.303R} - \frac{\Delta H_{corr}}{2.303RT} \tag{19}$$

$$\Delta G_{corr} = \Delta H_{corr} - T\Delta S_{corr} \tag{20}$$

$$\Delta G_{ads} = -2.303RT \log [55.5\ K_{ads}] \tag{21}$$

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{22}$$

$$\theta = -\frac{2.303 \log K}{2a} - \frac{2.303 \log C}{2a} \tag{23}$$

$$\log\left(C \times \frac{\theta}{1-\theta}\right) = 2.303 \log K + 2\,a\,\theta \tag{24}$$

$$\log\left(\frac{\theta}{C}\right) = \log K + x\log(1-\theta) \tag{25}$$

$$\log\left(\frac{\theta}{1-\theta}\right) = \log K + y\log C \tag{26}$$

$$\log\theta = \log K + n\log C \tag{27}$$

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 CORROSION INHIBITION

By definition, a corrosion inhibitor is a chemical substance that when added in small quantity to a corrosive environment, effectively decreases the corrosion rate (Raja *et al., 2014).* The efficiency of an inhibitor can be expressed by a measure of this improvement:

$$\text{Inhibitor efficiency}(\%) = 100\frac{(\mathrm{CR}_{\text{unnhibited}} - \mathrm{CR}_{\text{inhibited}})}{\mathrm{CR}_{\text{unnhibited}}}$$

Where $\mathrm{CR}_{\text{uninhibited}}$=corrosion rate of the uninhibited system

$\mathrm{CR}_{\text{inhibited}}$=corrosion rate of the inhibited system

Corrosion is an unwanted phenomenon therefore needs to be prevented or at least reduced, and this can be achieved among other methods by adding chemical substances or compound called inhibitors. These compounds prevent corrosion either by being adsorbed on the surface of metals or alloys or by forming a protective layer, or by causing the formation of insoluble complex (Bilgic, 2005). To replace the environmentally hazardous chromates several nonchromates have been used as corrosion inhibitors. Extract of plant materials top the list. The plant extracts are environmentally friendly, nontoxic and readily available. These extracts contain several organic compounds which have polar atoms such as O, N, P and S. They are adsorbed onto the metal surface through these polar atoms; protective films are formed. Adsorptions of these ingredients obey various adsorption isotherms. The films have been analyzed by many surface techniques such as FTIR, UV and SEM. Naturally occurring substances as inhibition of acid cleaning process has continued to receive attention as replacement for synthesized organic inhibitors. Investigations onto the corrosion inhibition effect of some local plants have proposed parts of economic plants as pickling inhibitor (Ekpe *etal,* 1994 and Loto, 1998). Not much has actually been achieved using these local plants compared to the extensive research on synthesized organic inhibitors especially N and S containing organic compounds (Monticelli *et al* 1993 ; Ita and Offiong, 2000).

In general, the efficiency of an inhibitor increases with an increase in inhibitor concentration (e.g., a typically good inhibitor would give 95% inhibition at a concentration of 0.008% and 90% at a concentration of 0.004%). A synergism or cooperation is often present between different inhibitors and the environment being controlled, and mixtures are the usual choice in commercial formulations. The scientific and technical corrosion literature has descriptions and lists of numerous chemical compounds that exhibit inhibitive properties. Of these only few are actually used in practice. This is partly because the desirable properties of an inhibitor usually extend beyond those simply related to metal protection. Considerations of cost, toxicity, availability and environmental friendliness are of considerable importance. Commercial inhibitors are available under various trade names and labels that usually provide little or no information about their chemical compositions. It is sometimes very difficult to distinguish between products from different sources because they may contain the same basic anticorrosion agent. Commercial formulations generally consist of one or more inhibitor compounds with other additives such as surfactants, film enhancers, de-emulsifiers, oxygen scavengers and so forth. The inhibitor solvent package used could be critical in respect to the solubility or dispersibility characteristics and hence the application and performance of the products. The use of inhibitors is one of the most practical methods for corrosion protection, a lot of literatures shows that many plant extracts have been used as corrosion inhibitors. (Olasehinde *et al.,* 2012) investigated the inhibition of mild steel corrosion in acid by peels of *Musa Sapientum* using weight loss method. The result shows that inhibition efficiency increases progressively as the concentration of the extract increases and as the reaction temperature increases from 30^0c to 60^0c, the inhibition efficiency of the extract on the mild steel also increases suggesting an increase in the corrosion rate. The result also shows that Longmuir and Temkin adsorption isotherms were found to be suitable for the experimental findings. (Uzoma *et al.,* 2012) also investigated the corrosion behaviour of mild steel in hydrochloric acid using ethanol extract of *Vitex donania*. The experimental methods used are gravimetric and thermometric and the results showed that the corrosion rate decreased as the concentration of the ethanol extract increases from 0.1 to 0.5 g/L and with decrease in temperature from 60 to 30 ^{0}C. The process was also found to obey Longmuir ($R^2 = 0.9953$) and Temkin ($R^2 = 0.8939$) isotherm and physical adsorption was proposed from the value of Gibbs energy ($\Delta G = -10.12$ kJ mol^{-1}) and activation energy (Ea = 72.93 kJ mol^{-1}). From the calculated values of surface coverage and inhibition efficiency (68.49 %), the extract was found to be a very good inhibitor.

Orubite-Okorosaye and Oforka, (2004) carried out a research on corrosion inhibition of zinc in HCl using *Nypa fruitcans Womb* extract and 1,5 – diphenylcarbazone using weight loss techniques. The study shows that maximum inhibition efficiency and surface coverage was obtained at an optimum concentration but increase in temperature decreased the inhibition efficiency at the temperature range of 30°C to 40°C. The data obtained from the study fits well into Langmuir adsorption isotherm and the phenomena of physical adsorption was proposed from the values of activation energy. Nnanna *et al. (*2011a) studied the inhibitive effect of leaf extract of *Euphorbia hirta* on aluminium corrosion in HCl and NaOH solutions gravimetrically at 30 and 60 °C. The result shows that the extracts functioned as effective inhibitors in acidic and alkaline solutions and also suppressed the corrosion reaction in both solutions. Iloamaeke *et al. (*2012) investigated the corrosion inhibition of mild steel using *Pterocarpus soyauxi*, (PS) using weight loss measurement at 30°C and 60°C. According to his findings, physical adsorption mechanism was proposed from the calculated values of thermodynamic parameters. The inhibition efficiency increased with an increase in inhibitor concentration as a result of the phytochemical constituents of the PS extract but decreased with temperature. The inhibition of corrosion of mild steel obeyed Temkin and Freundlich adsorption isotherms and fitted into first order reaction kinetics.

Muhammad *et al.* (2014) examined the adsorptive and inhibitive action of glutamic acid towards general and pitting corrosion of aluminium in HCl solution using weight loss, gasometric and thermometric methods. Glutamic acid was found to inhibit the corrosion of aluminium in HCl solution. The inhibition efficiency of glutamic acid decreased with increase in temperature, period of immersion and HCl concentration, but increased with increasing glutamic acid concentration. An adsorption characteristic of glutamic acid was also studied by Muhammad *et al.* (2014) and it was found that the process obeys physical adsorption. Thermodynamic parameters including; Ea = 47.58 kJ mol^{-1}, $Q_{(ads)}$ = -25.32 kJ mol^{-1}, $\Delta S_{(ads)}$ = -210 Jmol^{-1}, $\Delta H_{(ads)}$ = -69.25 kJ mol^{-1} and $\Delta G_{(ads)}$ = -11.25 for the adsorption process signifies a spontaneous process. While Langmuir, Frumkin, Flory-Huggins and El-Awardy isotherm adsorption models could be used to explain the mechanism of glutamic acid adsorption onto aluminium surface in HCl solution (R^2 = 0.990-0.999) .

Eddy *et al.* (2009) investigated the inhibition efficiency of some antibiotics against mild steel corrosion using weight loss and quantum chemical techniques. Values of inhibition efficiency obtained from weight loss measurements correlated strongly with theoretical values obtained through semi empirical calculations. High correlation coefficients were also obtained between inhibition efficiency of the antibiotics and some quantum chemical parameters, including frontier orbital: energy of highest occupied molecular orbital and energy of lowest unoccupied molecular orbital (EHOMO and ELUMO), dipole moment, log of polarizability (log P), total negative charge (TNC) and LSER parameters (critical volume and dipolar-polarisability factor), which indicated that the parameters affect the inhibition efficiency of the compounds. It was also found that quantitative structure activity relation (QSAR) can be used to adequately predict the inhibition effectiveness of these compounds.

Eddy and Ebenso (2010) studied the inhibitive and adsorptive properties of Penicillin G, Amoxicillin and Penicillin V potassium using gravimetric, gasometric and quantum chemical methods, and found that the compounds are good adsorption inhibitors for the corrosion of mild steel in HCl solution which indicated high correlation value (R^2 = 0.876-0.999). The concentrations ranges are 3-13.0 $\times10^{-4}$ M at temperature range 303-333 K that gives the efficiency of 99.70 % at 303K, at maximum inhibitor concentrations. The adsorption of the inhibitors on mild steel surface is spontaneous (ΔG = -1 to -2.62 kJ mol^{-1}), exothermic (ΔH = -20.95 kJ mol^{-1}) and supports the mechanism of physical adsorption. From density functional theory (DFT) results, the sites for nucleophilic attacks in the inhibitors are the carboxylic acid functional group while the sites for electrophilic attacks are in the phenyl ring. There was a strong correlation between theoretical and experimental inhibition efficiencies

Eddy *et al.* (2009) investigated the corrosion inhibition of ampicillin (AMP) and its synergistic combination with halides (KI, KCl and KBr) for the corrosion of mild steel in H_2SO_4 using gravimetric, gasometric, thermometric and infrared (IR) methods. They found that the inhibition efficiencies (78.15%, 89.96% and 29.25%, 75.24%) of AMP for the corrosion of mild steel increased with increase in concentration (3.0×10^{-4} to 13.0×10^{-4} M) but decreased with rise in temperature from 303 to 333 K. The adsorption of AMP on the mild steel surface was found to obey the Langmuir adsorption isotherm model. The combination of AMP with the halides (KI, KBr and KCl) enhanced the inhibition efficiency and adsorption behaviour of the inhibitor indicating synergism. The inhibition efficiency of AMP increased with increasing concentration and the adsorption of the inhibitor was spontaneous. Physical adsorption mechanism has been proposed from the thermodynamic data obtained. There was a significant correlation between the inhibition efficiency of AMP and some quantum chemical parameters ($R^2 = 0.96$) using the quantitative structure–activity relationship (QSAR) method.

James *et al.* (2007) investigated the action of pyridoxal hydrochloric (PXA) and pyridoxol hydrochloride (PXO) on the corrosion of mild steel in hydrochloride acid (HCl) solution using the weight loss and gasometric methods, and found that percentage inhibition efficiencies increase with the concentration of the inhibitors and decrease with increase in temperature. The efficiencies increase in the order PXO > PXA. The kinetic treatment of the results gave first order kinetics. The relative inhibitive efficiency of these compounds has been explained on the basis of structure dependent – electron donor properties of the inhibitors.

2.2 THE MECHANISM OF CORROSION INHIBITION

It has been established that the initial mechanism involved in any corrosion inhibition process is the adsorption of the inhibitor on the metal surface. This adsorption may be through charge transfer (physical adsorption) or donation and acceptance of electron(s) (chemical adsorption) (Wahyumingrum, *et al.*, 2008). This implies that corrosion inhibition process involves an electrophile (usually the metal) and nucleophile (usually the inhibitor) (Aramide, 2009).

Adsorption of corrosion inhibitors onto metals: The inhibitive efficiency is usually proportional to the fraction of the surface Θ covered with adsorbed inhibitor. However, at low surface coverage ($\Theta<0.1$), the effectiveness of adsorbed inhibitor species in retarding the corrosion reactions may be greater than at high surface coverage. In other cases, adsorption of inhibitors, such as thiourea and amines, from diluted solutions, may stimulate corrosion (El-Etre, 1998).

The information on inhibitor adsorption, derived from direct measurements and from inhibitive efficiency measurements, considered in conjunction with general knowledge of adsorption from solution, indicates that inhibitor adsorption on metals is influenced by the following main features (Noor, 2009b).

2.2.1 Surface Charge on the Metal

Adsorption may be due to electrostatic attractive forces between ionic charges or dipoles on the adsorbed species and the electric charge on the metal at the metal-solution interface. In solution, the charge on a metal can be expressed by its potential with respect to the zero-charge potential. This potential relative to the zero-charge potential, often referred to as the (ϴ- potential), is more important with respect to adsorption than the potential on the hydrogen scale, and indeed the signs of these two potentials may be different. As the potential of a metallic surface becomes more positive, the adsorption of anions is favoured and as the ϴ- potential becomes more negative, the adsorption of cations is favoured (Noor, 2009b).

2.2.2 The Functional group and Structure of the Inhibitor

Inhibitors can also bond to metal surfaces by electron transfer to the metal to form a coordinate type of link. This process is favoured by the presence in the metal of vacant electron orbital of low energy, such as occurs in the transition metals. Electron transfer from the adsorbed species is favoured by the presence of relatively loosely bounded electrons, such as may be found in anions and neutral organic molecules containing lone pair electrons or π-electron systems associated with multiple, especially triple bonds or aromatic rings. The electron density at the functional group increases as the inhibitive efficiency increases in a series of related compounds. This is consistent with increasing strength of coordinate bonding due to easier electron transfer and hence greater adsorption (Noor, 2009a, b).

2.2.3 Interaction of the Inhibitor with Water Molecules

Adsorption of inhibitor molecules is often a displacement reaction involving removal of adsorbed water molecules from the surface. During adsorption of a molecule the change in interaction energy with water molecules in passing from the dissolved to the adsorbed state forms an important part of the free energy change on adsorption. This has been shown to increase with the energy of salvation of the adsorbing species, which in turn increases with increasing size of the hydrocarbon portion of an organic molecule. Thus increasing size leads to decreasing solubility and increasing adsorbability. This is consistent with the increasing inhibitive efficiency observed at constant concentrations with increasing molecular size in a series of related compounds (Noor, 2009a, b).

2.2.4 Interaction of Adsorbed Inhibitor Species

Lateral interactions between adsorbed inhibitor species may become significant as the surface coverage and hence the proximity, of the adsorbed species increases. These lateral interactions may be either attractive or repulsive. Attractive interactions occur between molecules containing large hydrocarbon components (e.g. n-alkyl chains). As the chain length increases, the increasing vander waals attractive force between adjacent molecules leads to stronger adsorption at high coverage.

In the case of ions the repulsive interaction can be altered to an attractive interaction if anions of opposite charge are simultaneously adsorbed. In a solution containing inhibiting anions and cations, the adsorption of both ions may be enhanced and the inhibitive efficiency greatly increased compared to solution of individual ions. Thus, synergistic inhibitive effects occur in such mixtures of anionic and cationic inhibitors (El-Etre *et al.,* 2005).

2.2.5 Reaction of Adsorbed Inhibitor

In some cases, the adsorbed corrosion inhibitor may react, usually by electrochemical reduction, to form a product that may also be inhibitive. Inhibition due to the added substance has been termed primary inhibition and that due to the reaction product, secondary inhibition. In such cases the inhibitive efficiency may increase or decrease with time according to whether the secondary inhibition is more or less effective than the primary inhibition. Sulfoxides, for example can be reduced to Sulfides which are more efficient inhibitors (Lukovits and Kalman 2003).

2.3 THE INHIBITOR ANTIBIOTICS (*Ampiclox*)

The β-lactam group of antibiotics is by far the largest group of antibacterial agents used in clinical medicine. Structurally, all are based upon the four-membered nitrogen-containing β-lactam ring that gives these agents their antibacterial activity. They can be divided into four groups, i.e. penicillins, cephalosporins, carbapenems and monobactams, on the basis of the molecular structures surrounding and supporting this active site. Only two classes' of these antibiotics, penicillins and cephalosporins, will be considered in this review due to the lack of reported carbapenem or monobactam drugs as corrosion inhibitors (Eddy and Odoemelam 2008).

2.3.1 *The penicillins*

The original group of b-lactam antibiotics is the penicillins, whose target is the cell wall (De-Weck, 1983; Blumberg, 1974). There are 4 classes of penicillins, based upon their ability to kill various types of bacteria. The following are the penicillin classes which include the drugsused as corrosion inhibitors:

2.3.2 *Natural penicillins*

The natural penicillins (penicillin G, procaine, penicillin V, benzathine) were the first agents in the penicillin family to be introduced for clinical use. The natural penicillins are based on the original penicillin-G structure. Benzyl penicillin (penicillin G), the original member of the group, remains the most active antibacterial agent against sensitive bacteria. It is the drug of choice for serious infections. On the other hand, penicillin V is used for the treatment of streptococcal pharyngitis (Kirschbaum, 1986). It is also useful for anaerobic coverage in patients with oral cavity infections. Eddy *et al*. (2008), Eddy *et al*. (2009) pioneered research in the field of penicillins as mild steel corrosion inhibitors. They explained the inhibitory action of penicillin G and penicillin V in terms of their physical adsorption on the surface of mild steel.

2.3.3 *Penicillinase-Resistant Semisynthetic Penicillins*

Methicillin was the first member of this group, followed by oxacillin, nafcillin, cloxacillin and dicloxacillin. The penicillinaseresistant penicillins have a narrower spectrum of activity than the natural penicillins. Their antimicrobial efficacy is aimed directly against penicillinase-producing strains of gram-positive cocci, particularly staphylococcal species and these drugs are sometimes called *anti-staphylococcal penicillins* (Sabath *et al.,* 1975).

2.4 LOCAL PLANTS USED AS INHIBITORS

Corrosion inhibition of carbon steel in the presence of different concentrations of aqueous extract from henna leaves in 1 M HCl solution has been studied using the weight loss and potentio dynamic polarization methods. The effect of temperature on the corrosion behaviour of carbon steel was investigated in the temperature range 293-333 K. The inhibition efficiency increases with increasing inhibitor concentration but decreases with increasing temperature. The activation and free energies for the inhibition reactions support the mechanism of physical adsorption. The potentio dynamic polarization measurements indicate that henna extract acts as a mixed type inhibitor. Surface and protective film analysis have been carried out using; energy dispersive X-ray (EDX), scanning electron microscopy

(SEM), Fourier transforms infrared (FT-IR) spectroscopy and X-ray diffraction (XRD) analysis (Hamdy and Nour, 2012).

An aqueous extract of plant material Henna (*Lawsonia Inermis L*) powder has been used as a corrosion inhibitor in controlling corrosion of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^-, by the mass loss method in the absence and presence of Zn^{2+}. The main constituent of this plant extract is Lawsone. It has excellent inhibition efficiency (IE) and shows excellent IE at pH 6,8 and 12. In the presence of Zn^{2+} there exists a synergistic effect. Synergism parameters have been calculated to evaluate the synergistic effect. Analysis of variance (F-TEST) reveals that the synergistic effect existing between henna extract and Zn^{2+} in statistically significant. The protective film has been analyzed using Fourier transform infrared (FTIR) spectroscopy. The film consists of Fe^{2+} -Lawsone complex and Zinc hydroxide. It is found to be UV-fluorescent. Electrochemical studies such as potentio dynamic polarization and alternating current (AC) impedance have been used to find the mechanistic aspects of corrosion inhibition (Rajendran *et al*., 2009).

The inhibition potentials of lignin extract of sun flower was investigated by evaluating the corrosion behaviour of medium carbon low alloy steel immersed in 1M H_2SO_4 solution containing varied concentration of the extract. Mass loss, corrosion rate, and adsorption characterization were utilized to evaluate the corrosion inhibition and adsorption properties of the extract. The results revealed that the lignin extract is an efficient inhibitor of corrosion in mild steel immersed in 1M H_2SO_4. The corrosion rates were observed to decrease with increase in concentration of lignin extract but increase with temperature. The activation energies and the negative free energy of adsorption obtained from the adsorption studies indicate that the lignin extract is physically adsorbed on the surface of the steel and that the adsorption is strong, spontaneous and fit excellently with the assumptions of the Langmuir adsorption isotherm (Alaneme and Olusegun, (2012).

Corrosion inhibition effect on C38 steel of alkaloids extract from Palicourea guianensis plant (AEPG) in 1 M HCl medium has been investigated by potentio dynamic polarization and electrochemical impedance spectroscopy. The polarization studies showed that AEPG acts as mixed type inhibitor. The electrochemical impedance spectroscopy indicated that the charge transfer resistance increases and the double layer capacitance decreases on increasing plant extract concentration. The inhibition efficiency of the extract obtained from impedance and polarization measurements was in a good agreement and was found to increase with increasing concentration of the extract. Inhibition efficiency of 89% was obtained with 100 mg/L of AEPG at 298 K. The obtained results showed that, the *Palicourea guianensis* extract could serve as an effective inhibitor for the corrosion of steel in acid media. The adsorption of AEPG obeys the Langmuir adsorption isotherm (Lebrini *et al*, 2011).

The inhibition effect of *Atropa Belladonna* extract (ABE) on the corrosion of carbon steel in 1 M HCl solution was investigated by potentio dynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. The adsorption process obeyed a Langmuir adsorption isotherm. ABE acts as a mixed-type but mainly anodic inhibitor in 1 M HCl. The calculated adsorption thermodynamic parameters indicated that the adsorption was a spontaneous, exothermic process accompanied by an increase in entropy. The maximum inhibition approached 96.6% in the presence of 500 ppm ABE using Tafel polarization technique. Quantum chemical parameters were also calculated, which provided reasonable theoretical explanation for the adsorption and inhibition behavior of ABE on C-steel. ABE constituents have been simulated as adsorbate on Fe (1 1 0) substrate and the adsorption energy have been identified on iron surface. The results obtained from different electrochemical techniques and theoretical calculations were in good agreement (Shalabi et al, 2014).

The strict environmental legislations and increasing ecological awareness among scientists have led to the development of “green” alternatives to mitigate corrosion. In the previous work, literature on green corrosion inhibitors has been reviewed, and the salient features of the work on green corrosion inhibitors have been highlighted. Among the studied leaves, extract *Andrographi spaniculata* showed better inhibition performance (98%) than the other leaves extract. *Strychnos nuxvomica* showed better inhibition (98%) than the other seed extracts. *Moringa oleifera* is reflected as a good corrosion inhibitor of mild steel in 1M HCl with 98% inhibition efficiency among the studied fruits extract. *Bacopa monnieri* showed its maximum inhibition performance to be 95% at 600 ppm among the investigated stem extracts. All the reported plant extracts were found to inhibit the corrosion of mild steel in acid media (Singh *et al,* 2012).

The Inhibitive action of the extracts of *Adathoda vasica, Eclipta alba*, and *Centella asiatica* on the corrosion of mild steel in 1N HCl has been studied using weight loss method, electrochemical methods, and hydrogen permeation method. Polarization method indicates that the plant extracts are under mixed control that is, promoting retardation of both anodic and cathodic reactions. The impedance method reveals that charge-transfer process controls the corrosion of mild steel. The plant extracts obey Langmuir adsorption isotherm. Theoretical fitting of the corrosion data to the kinetic-thermodynamic model was tested to show the nature of adsorption. Physisorption mechanism has been proposed for the inhibition action of these plant extracts. The protective film formed on the surface was confirmed by SEM. From hydrogen permeation method, all the plant extracts were able to reduce the permeation current. Results obtained in all three methods were very much in good agreement in the order Eclipta alba > Adathoda vasica > Centella asiatica, and, among the three plant extracts studied, the maximum inhibition efficiency was found in Eclipta alba which showed

99.6% inhibition efficiency at 8.0% v/v concentration of the extract (Shyamala and Kasthuri, 2012).

Corrosion inhibition efficiency of dry Polyalthia longifolia (Asoka tree) leaves in 1N HCl medium was investigated by weight loss and temperature studies. Effect of temperature (35-75 ^{0}C) on the corrosion behaviour 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. The results obtained prove that the leaves of Polyalthia Longifolia act as a good corrosion inhibitor having efficiency of 87% at 1.5% inhibitor concentration (Vasudha and Shanmuga, 2013).

Corrosion inhibition of mild steel using *pterocarpus soyauxi,* (PS) was studied using weight loss measurement at 30^{o}C and 60^{o}C. The inhibition efficiency increased up to 96% with an increase in inhibitor concentration at 0.5 g/L but decreased with temperature to 63.55%. The inhibition of corrosion of mild steel obeyed Tempkin and Freundlich adsorption isotherms and fitted into first order reaction kinetics with almost unit value of R^2. Some thermodynamics parameters, such as Ea = 64.90 kJmol^{-1}, ΔH = -55.60 kJmol^{-1}, and ΔG = -9.98 kJmol^{-1}, were calculated and all indicated that inhibition of corrosion of mild steel by ethanol extract of PS was by physical adsorption mechanism (Iloamaeke *et al*, 2012).

The inhibitive effect of pulverized *Jatropha curcas* leaves on the corrosion of medium carbon steel in 0.5M NaCl and 0.5 M H_2SO_4 solutions was investigated by gravimetric method for monitoring corrosion rate. The leaves were dried and ground to powder. The concentration of the extract used ranges from 0.5 – 2.5 g in 300 ml of 0.5 M H_2SO_4 solutions.The inhibition efficiency of 92.1 % was obtained from the 1.5 g of the pulverized *Jatropha curcas* leaves in NaCl solution, while 55.5 % efficiency was obtained from 2.5 g extract in H_2SO_4 solution. The overall results obtained indicated that Jatropha curcas leaves extract could be used as inhibitor against the corrosion of medium carbon steel in both the alkaline and acid solutions.

The corrosion inhibition of aluminium in sulfuric acid solution in the presence of different plant parts, namely, leaves, latex, and fruit was studied using weight loss method and thermometric method. The ethanolic extracts of *Calotropis procera* and *Calotropisgigantea* act as an inhibitor in the acid environment. The inhibition efficiency increases with increase in inhibitor concentration. The plant parts inhibit aluminium, and inhibition is attributed, due to the adsorption of the plant part on the surface of aluminium (Kumar and Mathur, 2013).

Investigation of adsorptive and inhibitive effect of extracts of Alstonia boonei on aluminium corrosion in 1.0 M sulphuric acid by gravimetric technique gave inhibition efficiency of 59.6 and 47.7 % for 0.5 g/L concentration of the extracts at 303 and 333 K respectively. Gasometric measurement gave an inhibition efficiency of 61.0 and 49.9 % at 303 and 333 K respectively. Adsorption behaviour was best approximated by the Freundlich adsorption model with evidence of efficient adsorbate-adsorbent binding potential (K_{ads} = 0.325-0.442). The feasibility of the reaction was proposed from the trend of ΔG_{ads} = -26.0 to –39.3 kJmol^{-1} obtained and show that it is spontaneous. The adsorption of the extracts onto the metal surface was spontaneous and exothermic. The extracts increased the energy barrier (Ea) of the inhibited solution (2.93 kJ mol^{-1}) above that of the blank (3.58 kJ mol^{-1}) and hence the inhibition process (Ituen et al, 2013).

The inhibitive effect of leave extract of *Euphorbia hirta* on aluminium corrosion in HCl and NaOH solutions were studied using gravimetric technique at 30 and 60 ^{0}C. Results obtained indicated that the leaves extract functioned as effective and excellent inhibitors in the acidic and alkaline media. Also, the leaves extract suppressed the corrosion reaction in both media. Inhibition efficiency of the extract was found to vary with concentration, temperature and period of exposure. The leaves extracts of E. hirta showed better inhibition efficiency in the acidic medium than in the alkaline medium. The adsorption characteristics of the leaves extract were best described by the Langmuir isotherm. Values of the free energy of adsorption G_{ads} were determined from the isotherm parameters and they showed that the adsorption was spontaneous. The molecular interaction parameter (α) between the molecular species of the inhibitors and the metal surface they cover was also determined. The heat of adsorption (Q_{ads}) and apparent activation energy (Ea) were estimated from the temperature dependence of inhibition efficiency. Physical adsorption mechanism was proposed from the obtained thermodynamic parameters (Nnanna *et al,* 2011).

Corrosion inhibition of aluminium alloy (AA3003) in 0.5 M HCl by extracts of selected plants was investigated using gravimetric technique at 30 and 60 ^{0}C.The studied plant materials are extracts of Euphorbia hirta and Dialum guineense. The results showed that all the extracts inhibited the corrosion process in the medium by virtue of adsorption and inhibition efficiency increased with increase in concentration. Inhibition mechanisms were obtained from the temperature dependence of the inhibition efficiency as well as from activation parameters that govern the process. Adsorption of both plant extracts on the aluminium alloy was found to obey the Langmuir adsorption isotherm. The phenomenon of physical adsorption is proposed from the obtained thermodynamic parameters (Nnanna *et al*, 2010).

The corrosion inhibition of AA8011 aluminium alloy in acidic solutions using *Newbouldia leavis* leaf extract by way of gravimetric measurements was studied. It was shown that the presence of *Newbouldia leavis* leaf extract inhibited the corrosion of aluminium in the test solutions and the inhibition efficiency de-pended on the concentration of the plant extract as well as on the time of exposure of the aluminium samples in H_2SO_4 solutions containing the extract. The experimental data complied with the Langmuir adsorption isotherm and the value and sign of the Gibb's free energy of adsorption obtained suggested that inhibitor molecules have been spontaneously adsorbed onto the aluminium surface through a physical adsorption mechanism (Nnanna *et al*, 2011).

The inhibition of aluminium in 0.5 M H_2SO_4 by extracts of *Spondias mombin L.* was investigated using the standard gravimetric technique at 30–60 ^{0}C. The trend of inhibition efficiency with temperature was used to propose the mechanism of inhibition. It was found that the *S. mombin L.* extract acts as an inhibitor for acid-induced corrosion of aluminium. Inhibition efficiency (%I) of the extract increased with an increase in concentration of the S. mombin L. extract but decreased with temperature. Furthermore, inhibition efficiency (%I) synergistically increased on addition of potassium iodide. Inhibitor adsorption characteristics were approximated by Langmuir adsorption isotherm at all the concentrations and temperatures studied. The mechanism of physical adsorption is proposed from the trend of inhibition efficiency with temperature and from the calculated values of Gibbs free energy, activation energy and heat of adsorption. Quantum chemical calculations were performed using the density functional theory at B3LYP/6-31G (d) level of theory to find out whether a clear link exists between the inhibitive effect of the extract and the electronic properties of its main constituents (Obi-Egbedi et al, 2012).

The inhibition efficiency of extract of Garlic on aluminium in hydrochloric acid solutions has been evaluated by weight loss techniques. Values of inhibition efficiency obtained are dependent upon the concentration of inhibitor and temperature. Generally, inhibition was found to increase with inhibitor concentration, half-life, activation energy but decrease with temperature and first order rate constant at the temperatures studied. Physical adsorption mechanism has been proposed for the inhibition and Langmuir, Temkin adsorption isotherm was obeyed. Garlic is an inhibitor of aluminium corrosion in 0.5 M hydrochloric acid solution. The values of standard free energy of adsorption suggest that the adsorption of inhibitor on aluminium surface occurred by physisorption mechanism. The negative sign of the Free Energy of adsorption indicates that the adsorption of the inhibitors on the aluminum surface was a spontaneous process. The negative values of enthalpy of adsorption (H) suggest that the chemical reaction involved in the adsorption of the inhibitors on the metal surface is an exothermic process; hence increase in the reaction temperature of the medium will decrease the inhibition efficiency (Al-Mhyaw, 2014).

The efficacy and efficiency of *Bucolzia coriacea* (BC) and *Cninodoscolus chayans* (CC) plants extracts as corrosion inhibitors for aluminium pigments using gas volumetric technique was examined. The results obtained from this study indicate that all the extracts inhibited the corrosion process by extending the latency periods of the aluminium pigment-extract mix far beyond that of the bare aluminium pigment. Inhibition efficiency obtained was not only concentration dependent but also plant dependent and followed the order: BC > CC. A linear correlation was obtained between inhibition efficiency and duration of latency for each extract. Molecular modelling was used to evaluate the structure, electronic reactive parameters of the plant extracts in relation to their effectiveness as corrosion inhibitors (Akalezi *et al*, 2012).

The inhibitive action of leaf extracts of *Sansevieria trifasciata* on aluminium corrosion in 2M HCl and 2M KOH solutions was studied using the gasometric technique. The results indicate that the extract functioned as a good inhibitor in both environments and inhibition efficiency increased with concentration. Synergistic effects increased the inhibition efficiency in the presence of halide additives. Temperature studies revealed a decrease in efficiency with rise in temperature and corrosion activation energies increased in the presence of the extract. A mechanism of physical adsorption is proposed for the inhibition behaviour. The adsorption characteristics of the inhibitor were approximated by Freundlich isotherm (Oguzie, 2007).

The effect of *Morinda tinctoria* (MT) leaves extract on the corrosion inhibition of Al in acid medium was studied. The inhibition studies were carried out on Al in 0.5 mol / L HCl with the extract of leaves of MT using mass loss and electrochemical techniques. Parameters, such as concentration of the inhibitor, concentration of the acid, temperature and concentration of halide ions, were varied and optimized. Increase of the temperature and concentration of acid can decrease the performance of the inhibitor. Thermodynamic parameters show that the physisorption of the inhibitor molecules on Al surface obeys Langmuir isotherm (Krishnaveni and Ravichandran, 2014).

The inhibition of the corrosion of mild steel by acid extract of *Musa sapientum* peels in 1M HCl was investigated using weight loss method. The results showed that the corrosion rate of mild steel in 1M HCl decreases with increase in concentration of the extracts and the values were in the range 0.013021 - 0.002127 ghr^{-1}cm$^{-2.}$ The inhibition efficiency increases progressively as the concentration of the extracts increases up to about 4% (v/v), above which, further increase in extract concentration did not cause any significant change in the inhibition efficiency. Effects of temperature on the inhibition efficiency of the extracts showed that inhibition efficiency decreases with increase in temperature. Activation energy (Ea) was found to be 61.60 kJmol^{-1} for 1M HCl and increases to 66.72kJmol^{-1} in the presence of *Musa sapientum* extract. The values for enthalpy of activation and entropy were all positive indicating the endothermic nature of the mild steel dissolution process. Calculated Gibbs free energy was in the range -9.43 to -8.99kJmol^{-1}. Kinetics of the reaction in the presence of the extracts revealed that it follows a first order reaction and the half-life increases as the concentration of the extracts increases suggesting that inhibition efficiency increases with increase in the concentration of the extracts. Preliminary investigation of the phytochemical constituents showed that *Musa sapientum* contains tannin, flavonoid, terpenoid and some other compounds in trace constituents (Olasehinde *et al,* (2012).

The inhibitive action of ethanol extracts from leaves (LV), bark (BK) and roots (RT) of *Nauclea latifolia* on mild steel corrosion in H_2SO_4 solutions at 30–60 ^{0}C was studied using weight loss and gasometric techniques. The extracts were found to inhibit the corrosion of mild steel in H_2SO_4 solutions and the inhibition efficiencies of the extracts follow the trend: RT > LV >BK. The inhibition efficiency increased with the extracts concentration but decreased with temperature rise. Physical adsorption of the phytochemical components of the plant on the metal surface is proposed as the mechanism of inhibition. The adsorption characteristics of the inhibitor were approximated by the thermodynamic-kinetic model of El-Awady (Uwah *et al*, 2013).

Inhibition effect of *Chlorophytum borivilianum* root extract (CBRE) on mild steel corrosion in 1 M HCl and 0.5 M H_2SO_4 media has been studied using various techniques, viz., weight loss, electrochemical impedance spectroscopy, Tafel polarization, and scanning electron microscopy. Results indicate that inhibition efficiency of CBRE increases with an increase in inhibitor concentration in both acid media. Furthermore, the effect of immersion time (120 h), temperature (35−55 °C), and acid concentration on the inhibition potential of CBRE has been investigated by weight loss method. Characterization of CBRE was carried out using Fourier transform infrared spectroscopy, UV− visible spectroscopy, and preliminary phytochemical screening tests. The Langmuir isotherm model is proposed as the most suitable adsorption isotherm in both acid solutions. The UV− visible study and scanning electron microscopy images have confirmed the molecular adsorption of the extract on a mild steel surface. Results of the techniques used are in good agreement and reflect the potential of the extract for corrosion inhibition of mild steel in acidic environments (Gopal *et al*, 2013).

The experimental aspect of the corrosion inhibition potentials of *Boscia senegalensis* was carried out using gravimetric and linear polarization techniques as well as scanning electron microscopy and Fourier transform infrared spectroscopy (FTIR), whereas the theoretical aspect was studied using the density functional theory calculations to be performed and modelling the electronic structures of some extract constituents, including physiosorptive interactions with the Fe surface. The analyses of the experimental results showed that the inhibition efficiency increased with increase in concentration of the inhibitor and decreased with increase in temperature. The efficiency of the extract in HCl was 70%. Thermodynamic parameters revealed that the adsorption of extract onto the metal surface was spontaneous, exothermic, and supported the physical adsorption process. FTIR results showed that the inhibition mechanism was an absorption process through the functional groups present in the extract and that of the inhibited. Surface morphology also revealed that corrosion product confirmed the protection offered by the extract on the surface of the metal immersed in the acid media. The data obtained were fitted into various adsorption isotherms, though the Freundlich isotherm was found to be the best fit (Awe et al, 2015).

Corrosion is a costly and complicated problem facing mild steel utility. This study investigated the use of ethanol extract of *Vitex doniana* as a corrosion inhibitor for mild steel in HCl medium. Experimental methods used are gravimetric and thermometric. The results showed that corrosion rate decreased as the concentration of ethanol extract of *Vitex doniana* increased and with decrease in temperature. *Vitex doniana* extract obeyed Langmuir and Temkin adsorption isotherm. Physical adsorption was proposed from ΔG and Ea. Inhibition efficiency (I%) and the degree of surface coverage (θ) were calculated and all indicated that *Vitex doniana* was a good corrosion inhibitor (Uzoma et al, 2012).

The inhibition effect of unripe fruit peel extract of *Musa acuminate* (Cultivar variety – Nendran) (MNP) on corrosion of mild steel in 1 N HCl has been investigated by weight loss and electrochemical impedance spectroscopy (EIS) with various concentrations of the extract. The effect of temperature on the corrosion inhibition of mild steel in the temperature range of 30°C – 80°C was carried out. The result indicate that MNP extract act as an effective inhibitor in the acid environment and is of mixed type inhibitor having efficiency as high as 96% at 2% inhibitor concentration. The inhibition efficiency of MNP extract increases with the increase of concentration but decreases with the increase in temperature. The inhibitor achieves its inhibition by physical adsorption of nutrients of the peel extract on the surface of the mild steel. The experimental data revealed that the adsorption occurred according to the Langmuir and Temkin adsorption isotherm (Gunavathy and Murugavel, 2011).

Ethanols extract of *Vernonia amygdalina* was used to study the inhibitive, thermodynamics and adsorptive properties for the corrosion of mild steel in 0.4M HNO_3 solutions using weight loss technique. The extract was found to be a good inhibitor for the corrosion process. Inhibition efficiencies deduced ranged from 40.57- 50.74% and from 38.06 – 49.27% at 303 and 323K respectively. The inhibition efficiency of the extract decreased as temperature and time of immersion increased but increased with increase in concentration of extract. The inhibition ability of this extract is attributed to the presence of saponnin, tannin, alkaloid, anthraquinone, flavonoid, and cardiac glycosides in the extract (Nwabanne and Okafor 2011). The mechanism of physical adsorption was proposed from thermodynamics parameters.

The corrosion inhibition of zinc in hydrochloric acid by extract of *Nypa Fruticans* Wurmb was investigated using weight loss technique. Maximum inhibition efficiency and surface coverage were obtained at an optimum concentration. However, increased in temperature decreased the inhibition efficiency at the temperature range studied. The inhibition action of *Nypa Fruticans Wurmb* extract compared closely to that of 1, 5 Diphenyl Carbazone (DPC). Optimum inhibition efficiency for zinc in the presence of *Nypa Fruticans* Wurmb extract was 36.43% and 40.70% with DPC. The phenomenon of physical adsorption has been proposed from the activation energy values ($19.33kJmol^{-1}$ and $21.11kJmol^{-1}$) with *Nypa Fruticans* Wurmb extract and DPC respectively. A first order kinetics has been deduced from the kinetic treatment of the results. The heats of adsorption, the mean gibb's free energy of adsorption are suggestive of adsorption on metal surface. The data obtained from the study fits well into the Langmuir isotherm. Evidence indicated that *Nypa Fruticans* Wurmb extract and DPC inhibits the corrosion of zinc comparatively (Okorosaye and Oforka, 2004).

The inhibition of the corrosion of zinc by acetone extract of red onion skin in hydrochloric acid solutions has been studied using weight loss method. The results of this study revealed that different concentrations of the extract inhibit zinc corrosion. Inhibition efficiency of the extract is found to vary with concentration and temperature. The active ingredient in red onion skin is Quercetin. Acetone extract of red onion skin could serve as an effective and non-toxic inhibitor of the corrosion of zinc in hydrochloric acid solution (James and Akaranta, 2009).

The effect of the extract of *Aloe vera* leaves on the corrosion of zinc in 2 M HCl solution was studied using weight loss technique. *Aloe vera* extract inhibited the corrosion of zinc and the inhibition efficiency increased with increasing concentration of the extract but decreased with increasing temperature. The adsorption of the inhibitor molecules on zinc surface was in line with Langmuir adsorption isotherm. A first-order kinetics relationship with respect to zinc was found with and without the extract from the kinetics treatment of the data (Abiola and James, 2010).

The inhibitive action of the extract of *Ficus nitida* leaves toward general and pitting corrosion of C-Steel, Nickel and Zinc in different aqueous media was studied using Weight loss, Potentio static and Potentio dynamic polarization method. It was found that the presence of Ficus extract in the corrosive environment (acidic, neutral or alkaline) decreases the corrosion rates of the three tested metals. The inhibition efficiency increases as the extract concentration is increased. The inhibition efficiency depends on the type of corroded metal and on the corrosive solution. It was also found that the presence of *Ficus* extract in the chloride containing solution shifts the pitting potentials of the tested metals toward the noble direction. The inhibitive action of the extract was discussed with respect to the adsorption of its components; the poly atomic compounds, friedelin, epifriedelanol and nitidol on the metal surface. All the adsorption was found to obey Langmuir adsorption isotherm. The calculated values of the free energy of adsorption indicated that the adsorption phenomenon is spontaneous (El-Etre and El-Tantawy, 2006).

Researched reported the application of plant extracts for metallic corrosion control on the inhibiting effect of the *Aniba rosaeodora* alkaloidic extract on the corrosion of C38 steel in 1 M HCl solution. Potentio dynamic polarization and electrochemical impedance spectroscopy techniques were used to study the metal corrosion behaviour in the absence and presence of the inhibitor. Phytochemical studies were carried out to investigate the phytochemical constituents and to determine the active molecule. XPS was also carried out to establish the mechanism of corrosion inhibition of the active molecule of C38 steel in acid solution. The inhibitor extract acted as an efficient corrosion inhibitor in 1 M HCl. Polarization studies showed that the Aniba rosaeodora alkaloidic extract was a mixed type inhibitor and its inhibition efficiency increased with the inhibitor concentration. The phytochemical constituents of the total alkaloids extract shows that it contains the anibine as the major alkaloid. The results obtained from the electrochemical study have clearly showed that the inhibition efficiency of the total extract was due to the presence of anibine. The XPS studies showed the formation of inhibitor layer containing the *Aniba rosaeodora* alkaloidic extract and the anibine molecules (Chevalier *et al*, 2014).

Azadirachta indica (AZ), commonly known as Neem was identified as green corrosion inhibitor for metals especially for mild steel, aluminium and tin. The plant extracts were applied for metallic corrosion inhibition by investigating the inhibiting properties of *A.*

indica using different techniques. The corrosion inhibition and adsorption properties of neem leaves extract in nitric acid solutions using a gravimetric technique was conducted at 30 and 60 ^{0}C.The aqueous neem leaves extract was found to be an excellent potential corrosion inhibitor for carbon steel in 1.0 M HCl using weight loss technique. AZ had a better effect with an inhibition efficiency of 85% at 30 ^{0}C and concentration of 0.25 g/l for stainless steel. The rate of corrosion increases with the increase in acid concentration and temperature. The inhibitor adsorption on steel followed Langmuir isotherm. Polarization study indicates the inhibitor functions as a mixed inhibitor (Sharma *et al*, 2015).

Plectranthus tenuiflorus (Shara) plant was investigated as safe (green) inhibitor on the corrosion of mild steel in 2.0 M H_2SO_4 solution using weight loss and hydrogen gas evolution technique. The results showed that Shara plant aqueous extract is good inhibitor for mild steel in this medium. The inhibition efficiency increases with the inhibitor concentration and decreases with rising temperature. The inhibition is attributed to adsorption of the inhibitor molecules onmild steel surface. Adsorption characteristics of the aqueous extract of Shara plant wereapproximated by Langmuir adsorption isotherm. Effect of temperature was studied in the range (30-70) º C and determination of activation parameters was also discussed (Al-Turkustani and Al-Marhabi, 2012).

Anti corrosion activity of *Tiliacora acuminate* leaf extract (TALE) as a corrosion inhibitor in 1 M HCl has been investigated using mass loss, potentio dynamic polarization, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), UV-Visible spectroscopy and X-ray diffraction (XRD) studies. The mass loss results show that TALE is an excellent corrosion inhibitor. The inhibition efficiency increases with increasing the temperature from 308 to 333 K, reaching a maximum value of 93.02 % at the highest concentration of 320 ppm at the temperature of 333 K. Polarization measurements revealed that the TALE acts as a mixed type inhibitor. Nyquist plot illustrates that on increasing TALE concentration, the charge transfer increases and the double layer capacitance decreases. The adsorption of TALE on mild steel obeys Langmuir adsorption isotherm. SEM studies confirm the adsorption of TALE on the mild steel surface (Karthik *et al*., 2015).

The inhibition of corrosion of mild steel using Paniala (*Flacourtia jangomas*) extract in 1 M HCl and 0.5 M H_2SO_4 solutions was investigated by weight loss method at 30^0C. The result showed that corrosion rate was significantly decreased in presence of the extract and inhibition efficiency increased with increasing the concentration of extract. In case of HCl maximum inhibition efficiency (98%) was found at 5% v/v inhibitor concentration and no considerable change in inhibition efficiency was observed after this concentration and in 0.5M H_2SO_4, it was found to be 95% efficiency at the same concentration of inhibitor. At lower concentration of inhibitor, better inhibition was observed in HCl medium as compared to H_2SO_4. The decreased corrosion rate was due to adsorption of plant extract which was discussed on the basis of Langmuir and Freundlich adsorption isotherm. Adsorption of *Flacourtia jangomas* depends on its chemical composition which showed the presence of various compounds like flavonoids, steroids, tannins and phenolic compounds with oxygen atoms and lone pair electrons for co-ordinate bonding with metal (Hasan and Sisodia, 2011).

Weight loss technique has been used to study the corrosion inhibition efficiency of tin in HNO_3 solution by using the leaves and stem extract of different varieties of Holy Basil viz. *Ocimum basilicum* (E_B), *Ocimum cannum* (E_C) and *Ocimum sanctum* (E_S). The results showed that all the varieties under study are good corrosion inhibitors, among which leaves extract of E_B is the most effective. Corrosion inhibition efficiency increases with increasing concentration of inhibitor and it also increases with increasing concentration of HNO_3 solution. Inhibition efficiency was found maximum up to 96.19% for tin with 0.6% leaves extract (Kumpawat *et al,* 2012).

2.5 SYNTHESIZED ORGANIC COMPOUNDS AS INHIBITORS

2-Pentadecyl-1,3-imidazoline (PDI), 2-Undecyl- 1,3-imidazoline (UDI), 2Heptadecyl-1,3-imidazoline (HDI), 2-Nonyl-1,3-imidazoline (NI) were synthesized and characterized by FT-IR and NMR Studies. The corrosion inhibition properties of these compounds on aluminium in 1 M HCl and 0.5 M H_2SO_4 were investigated by weight loss, potentio dynamic polarization, electrochemical impedance and scanning electron microscopic techniques. The weight loss study showed that the inhibition efficiency increases with increase in the concentration of the inhibitor and was found to be inversely related to time and temperature while it shows no significant change with increase in acid concentration. The effectiveness of these inhibitors were in the order of UDI > NI > PDI > HDI .The values of activation energy, free energy of adsorption, heat of adsorption, enthalpy of activation and entropy of activation were also calculated to elaborate the mechanism of corrosion inhibition. The adsorption of these compounds on aluminium surface follows the Langmuir adsorption isotherm. The potentio dynamic polarization data show that the compounds studied are mixed type inhibitors. Electrochemical impedance was used to investigate the mechanism of corrosion inhibition. The surface characteristics of inhibited and uninhibited metal samples were investigated by scanning electron microscopy (SEM) (Quraishi and Rafiquee, 2007).

The corrosion inhibition and adsorption characteristics of three selected imidazole derivative namely, 2-amino-4,5-imidazoledicarbonitril (AID),5-amino-4 imidazolecarboxamide (AIC) and imidazole (IM) on aluminium in 1.0 M HCl was investigated at 25 ^{0}C. Measurements were carried out under various experimental conditions using chemical (weight loss), and electrochemical (Tafel polarization and impedance) methods. Molecular dynamics (MD) method and density functional theory were also applied here for theoretical study. Results obtained showed that inhibition efficiency of these compounds increases with increase in their concentrations due to the formation of a surface film on the aluminum surface.

Adsorption energy as well as hydrogen bond length calculations showed that AID was the best corrosion inhibitor among the tested imidazol derivatives. Polarization measurements reveal that the selected imidazole derivatives function mainly as cathodic type inhibitors. Physisorption, followed by chemisorption was proposed as the mechanism for the inhibition process. Adsorption via H-bond formation was also considered here. Results obtained from theoretical study were found to confirm experimental findings (Khaled and Amin, 2009).

The corrosion inhibition of aluminum in NaOH in the presence of polyvinyl alcohol (PVA) at 30 and 40^0C and the effect of addition of halides (KCl, KBr, KI) were studied using weight loss and hydrogen evolution methods. Results obtained showed that PVA acts as a corrosion inhibitor in the alkaline environment. The inhibition efficiency increased with increase in concentration of PVA and synergistically increased on the addition of the halides but however decreased with rise in temperature. The phenomenon of physical adsorption is proposed from the obtained Ea and Q_{ads} values. PVA was found to obey Freundlich and Frumkin adsorption isotherms. The increase in inhibition efficiency I(%), surface coverage y values as well as synergistic parameter, (SI) were found to be in the order I^-> Br^-> Cl^- which clearly indicates that the radii and electronegativity of the halides play a significant role in the adsorption process (Umoren *et al*, 2007).

A Succinyl amide Gemini surfactant was synthesized using simple reaction mechanism from the seed oil of *Adenopus breviflorus* and applied as corrosion inhibitor of mild steel in 0.5M HCl via weight loss method. The process was monitored and confirmed using FTIR and NMR. The inhibitive mechanisms of succinyl amide Gemini surfactant was studied by scanning electron microscopy (SEM) pictures. The adsorption was found to be spontaneous, exothermic and obey Langmuir isotherm with the process being physisorption. The result of the corrosion study has proved that Succinyl amide Gemini surfactant from the seed oil of A breviflorus is an efficient inhibitor of mild steel corrosion in 0.5M HCl where it gave highest percentage inhibitor efficiency 94% at 298K, 92% at 308K and 64% at 318K at higher concentration of inhibitor of 160 mol/L (Adewuyi *et al,* 2014).

The inhibition and the effect of temperature and concentration of trans-4-hydroxy-4_-stilbazole on the corrosion of mild steel in 1M HCl solution was investigated by weight loss experiments at temperatures ranging from 303 to 343 K. The studied inhibitor concentrations were between 1×10^{-7} M and 1×10^{-3} M. The percentage inhibition increased with the increase of the concentration of the inhibitor. The percentage inhibition reached about 94% at the concentration of 1×10^{-3} M and 303 K. On the other hand, the percentage inhibition decreased with the increase of temperature. Using the Temkin adsorption isotherm, the thermodynamic parameters for the adsorption of this inhibitor on the metal surface were calculated. Trans-4-hydroxy-4_-stilbazole was found to be a potential corrosion inhibitor since it contained not only nitrogen and oxygen, but also phenyl and pyridine rings that are joined together with a double bond (–C=C–) in conjugation with these rings (Nahle *et al*, 2012b).

Four new corrosion inhibitors namely, 5-(3-phenyl allylidene) pyrimidine-2,4,6-trione (PPT), 5- (2-hydroxy benzlidene) pyrimidine-2,4,6-trione (HPT), 5- benzylidene pyrimidine-2,4,6-trione (BPT) and 5-(4-nitrobenzylidene) pyrimidine-2,4,6-trione (NPT) were synthesized and their inhibiting effect on corrosion of mild steel in 1M HCl was investigated using electrochemical impedance spectroscopy (EIS), Tafel polarization and weight loss measurements. The adsorption of the inhibitors obeyed Langmuir isotherm. Polarization curves indicated that the inhibitors are of mixed type (Quraishi *et al*, 2012).

The behaviour of tin metal in tartaric acid solution of different concentrations was investigated by electrochemical method. Some amino acid such as alanine, glycine, glutamic acid and histidine were used as environmentally safe inhibitors. The metal surface was examined via scanning electron microscopy (SEM). The E/I curves showed that the anodic behaviour of tin exhibits actives/passive transition. The active dissolution of tin was increased by increasing tartaric acid concentration. Glycine was found to give the highest corrosion inhibition efficiency at a concentration of 0.02mol/L. The corrosion inhibition process is based on the adsorption of the amino acid molecules on the metal surface. The adsorption process was found to obey the Freundlich isotherm and the adsorption of glycine on tin has an adsorption free energy of 1 0.2 kJ/mol which reveals physical adsorption of the amino acid molecules on the metal surface. The experimental impedance data are in good agreement with the polarization experiments. An equivalent circuit model was proposed for fitting of the experimental impedance data and to stimulate the electrode/ electrolyte interface. The inhibition efficiency of glycine (69.6%) showed that it is a good inhibitor El-Sherif and Badawy, 2011).

4, 5-Diphenyl-1H-Imidazole-2-Thiol (DIT) has been evaluated as a corrosion inhibitor for C38 steel in 1 M HCl by gravimetric method. The effect of DIT on the corrosion rate was determined at various concentrations. The effect of the temperature on the corrosion behaviour with addition of the optimal concentration of DIT was studied in the temperature range 298 – 328 K. The DIT acts as an effective corrosion inhibitor for C38 in hydrochloric acid medium. The inhibition process is attributed to the formation of an adsorbed film of DIT on the metal surface which protects the metal against corrosion. The protection efficiency increased with increase in temperature. Adsorption of DIT on the C38 steel surface is found to obey the Langmuir adsorption isotherm. Some thermodynamic functions of dissolution processes were also determined (Hmamou Ben *et al*, 2012).

The inhibition efficiency of Caffeine in controlling corrosion of carbon steel immersed in 60ppm of Cl^- ion environment has been evaluated in the absence and presence of Mn^{2+} ions by weight loss method. Influence of sodium dodecyl sulphate, pH and immersion period on the inhibition efficiency of the caffeine-Mn^{2+} ion system has also been investigatyed. The protective film formed on the metal surface has been analysed by FTIR Spectra. The protective film contained Fe^{2+}-Caffeine complex and $Mn(OH)_2$ (Anthony *et al,* 2004).

The adsorption and corrosion inhibition properties of caffeine as an eco-friendly corrosion inhibitor for mild steel in acid medium were investigated by electrochemical and spectroscopic methods. Polarization experiments showed that caffeine behaves as a cathodic type inhibitor. Impedance data showed that surface coverage increased with caffeine concentration in the range of 1.0-10.0 mmol/L. The maximum inhibition efficiency obtained was 92.4%. The adsorption of corrosion inhibitor was consistent with the Frumkin adsorption isotherm with a free energy of adsorption of -66.1 kJ/mol. Contact angle measurements revealed the formation of a hydrophobic protective film while scanning electron microscopy, energy dispersive spectroscopy and fluorescence experiments clearly verified the presence of caffeine on the surface of the metal (Fernando *et al*, 2014).

Corrosion inhibition of mild steel in 1 M HCl was investigated in the absence and presence of different concentrations of Caffeine. Weight loss, potentio dynamic polarization and electrochemical impedance spectroscopy methods were employed. Impedance measurements showed that the double-layer capacitance decreased and charge-transfer resistance increased with increase in the inhibitor concentration and hence increasing in inhibition efficiency. Potentio dynamic polariztion study indicated that the inhibitor act as Cathodic type inhibitor. The inhibitor was adsorbed on the steel surface according to the Langmuir adsorption isotherm model and quantum calculation parameters. It was concluded that the high corrosion inhibition efficiency of Caffeine was associated with its strong adsorption as a barrier film on the mild steel surface. Inhibitor efficiencies values obtained from various methods used are in good agreement (Youssoufi et al, 2013).

The corrosion inhibition properties of piroxicam (PRX) for mild steel corrosion in HCl solution were analysed by electrochemical impedance spectroscopy (EIS), potentio dynamic polarization and gravimetric methods. Physical adsorption is proposed for the inhibition and the process followed the Langmuir adsorption isotherm. The mechanism of adsorption inhibition and type of adsorption isotherm were proposed from the trend of inhibition efficiency with temperature, E_a and ΔG_{ads} Potentio dynamic polarization study clearly revealed that piroxicam acted as mixed type inhibitor. The experimental data showed a frequency distribution and therefore a modelling element with frequency dispersion behaviour, a constant phase element (CPE) has been used (Singh and Quraishi, 2010).

The inhibitive effect of 4-(N, N-dimethylamino) benzaldehyde thiosemicarbazone (DMABT) on the corrosion of mild steel (MS) in 1 N HCl and 1 N H_2SO_4 solutions was investigated by weight loss, potentio dynamic polarization and electrochemical impedance spectroscopy techniques. It is inferred on the basis of the obtained results that DMABT is a mixed type inhibitor, predominantly decreasing the cathodic reaction in both acidic media through adsorption on a MS surface. Adsorption obeys Langmuir adsorption isotherm in both acidic media. The observations regarding energy-dispersive X-ray, scanning electron microscopy and atomic force microscopy confirm the existence of a protective film of the inhibitor on a MS surface. The molecular adsorption of DMABT was ascertained by density functional theory data (Mourya *et al,* 2013). The corrosion inhibition of mild steel in 1 M HCl solution by a synthesized compound (3-benzoylmethyl benzimidazolium hexafluoroantimonate) was investigated electrochemically and by weight loss experiments. The concentration of this inhibitor ranged from 0.5M to 1M. The effect of temperature (from 303 to 343 K) and concentrations (from 0.5M to 1M) were investigated. The percentage inhibition increased with the increase of the concentration of the inhibitor and reached about 98% at the concentration of M at 303 K. The percentage inhibition decreased with the increase of temperature. The thermodynamic parameters for the adsorption of this inhibitor on the metal surface were calculated. This compound was found to be a very good corrosion inhibitor due to the presence of nitrogen in benzimidazole and phenyl ring (Nahle *et al*, 2012a).

Tafel polarization method was used to assess the corrosion inhibitive and adsorption behaviours of amino-tris (methylenephosphonic) acid (ATMP) for C38 carbon steel in 1 M HCl solution in the temperature range 30 to 60 ^{0}C. It was showed that the corrosion inhibition efficiency was found to increase with increasing in ATMP concentration but decreased with temperature which is suggestive of physical adsorption mechanism. The adsorption of the ATMP onto the C38 steel surface was found to obey Langmuir adsorption isotherm model. The corrosion inhibition mechanism was further corroborated by the values of kinetic and thermodynamic parameters obtained from the experimental data (Labjar *et al*, 2011).

The synergistic influence caused by iodide ions on the inhibition of corrosion of C-steel in 1M H_2SO_4 in the presence of some aliphatic amines has been studied using weight loss, potentio dynamic polarization method. Aliphatic amines were able to inhibit the corrosion of C-steel and the inhibition efficiency increases by increasing the concentration of the inhibitor and also by addition of iodide ions. Novel corrosion inhibitors such as Pyrrolidin-2-one (P5) and acetic acid (P4) were synthesized and tested as corrosion inhibitors for steel in 0.5M H_2SO_4. The study was carried out by weight loss, Potentio dynamic polarisation and electrochemical impedance spectroscopy (EIS) techniques. The inhibition efficiency increases with the concentration of P5 to attain 89% at 0.005M. Polarisation measurements show also that the pyrrolidones act as cathodic inhibitors (Abd El-Maksoud, 2008). A non-ionic surfactant, Octylphenol polyethylene oxide (OPPEO) was investigated as an inhibitor for corrosion of low-carbon steel in 0.5M H_2SO_4. The study was carried out by potentio dynamic and potentio static methods and scanning electron microscopy were used to study the inhibition effectiveness of the surfactant. The inhibition efficiency was found to increase with the inhibitor concentration and decrease with temperature. OPPEO showed higher constant protection efficiency near it critical micelle concentration. The activation energy of corrosion was found to be higher in presence than in absence of the inhibitor. The Gibbs energy of adsorption decreases with the temperature. The experimental data were fitted with the Flory-Huggins isotherm. Three water soluble surfactants based on maleic anhydride-oleic acid adduct (MO) were synthesized. These are triethanol ammonium salt of MO adduct (TEASMO), triethanolamine ester of MO adduct (TEAEMO) and polyoxyalkylated MO adduct (POAMO-23). FTIR and IH NMR confirmed chemical structures. The inhibitive efficiency of corrosion on mild steel in 1 M H_2SO_4 for these surfactants was found by potentio dynamic technique. The surface and thermodynamic properties of the surfactants were also investigated. The obtained data show that TEASMO exhibit minimum inhibition efficiency (65%), on the other hand, the maximum inhibition efficiency obtained was 95% with POAMO-23 (Abd El-Maksoud, 2008).

Electrochemical investigations were carried out to study the corrosion behaviour of tin plate in citric acid, in the absence and presence of various concentrations of amino acids by using potentio dynamic polarization technique. The results of this study revealed that nitrogen containing amino acids gave inhibition efficiency greater than 70% at 5ppm and sulphur containing amino acid gave 56% at 50ppm (Quraishi et al, 2004).

Stress corrosion cracking of aluminium brass in non-ammoniacal acidic chloride solutions has been studied by electrochemical method. The most intense transgranular penetration was found in the range of active potentials in synthetic sea water containing 1.5 g/l. of CuC1 at pH 1.5, in 1M sodium chloride solution containing 1.5 g/L of CuC1 at pH 2.0 and in 1M sodium chloride + 0.25M tri-sodium citrate solution containing 1.5 g/L of CuC1 at pH 4.0. Experimental evidence showed that high As and high P contents in the alloy can play an important role on the morphology and on the intensity of the corrosion process is presented.

2.6 FTIR AND SEM OF HENNA AND CAFFEINE

From the result evaluated by Anthony *et al,* (2004), the FTIR spectra of pure caffeine was interpreted to show C=O stretching frequency at 1658 cm^{-1}. The bands due to aromatic C-H stretch appear at 3111.4 and 2953.88 cm^{-1}. The band at 1484.5 cm^{-1} is due to C=N ring stretching. The CH_3 group absorptions in CH_3 –N appear at 1403 and 1429.8 cm^{-1}.

The FTIR spectrum of the film formed on the metal surface after immersion in the solution consisting of 60 ppm of Cl- and 75 ppm of Caffeine was also observed as the C=O stretching frequency has decreased from 1658 to 1632 cm^{-1}. This is due to the shift of the electron cloud of C=O bond towards Fe^{2+} ion formed on mild steel metal surface. This results in the formation of caffeine Fe^{2+} complex on the metal surface. The C=N ring stretching has decreased from 1484.5 cm^{-1} to 1454 cm^{-1}. This suggests that the electron cloud of C=N bond coordinates with Fe^{2+} ion formed on the metal surface. Thus, FTIR spectral study leads to the conclusion that in the presence of Cl^- and Caffeine, the anodic reaction of metallic dissolution was controlled by the formation of Caffeine – Fe^{2+} complex on the anodic sites of the metal surface. Caffeine was coordinated to Fe^{2+} through the oxygen atom of the C=O group and the ring nitrogen.

The presence of the film and Caffeine on the mild steel surface was further confirmed by SEM imaging and EDS composition analysis, respectively. The SEM and EDS data showed that a carbonaceous material containing oxygen atoms covered the steel surface. This protective layer was attributed to the inhibitor. Therefore, surface analysis by SEM and EDS support the results obtained by different techniques (Fernando *et al*, 2014).

Aqueous extract of Henna leaves was used as corrosion inhibitor in controlling corrosion of Carbon steel in the weight loss experiment study by (Rajendran *et al,* 2009). The main constituent of Henna extract is Lawsone. It contains benzene unit, p-benzoquinone unit and phenolic group. The Henna extract was evaporated to dryness to get a solid mass and its FTIR spectrum was identified. The phenolic O-H stretch appeared at 3437 cm^{-1}. The aromatic C=C stretching frequency appeared at 1514 cm^{-1}, the C=O stretching frequency appeared at 1624 cm^{-1}. Thus lawsone was characterized by IR spectroscopy.

The FTIR spectrum of the protective film formed on the surface of the metal after immersion in the solution containing 60 ppm of Cl^-, 50 ppm of Zn^{2+} and 2ml of Henna extract was observed. It was found that the phenolic O-H stretch has shifted from 3437 cm^{-1} to 3346 cm^{-1}. The aromatic C=C stretching frequency has shifted from 1514 cm^{-1} to 1504 cm^{-1}. The C=O stretching frequency has shifted from 1624 cm^{-1} to 1655 cm^{-1}. It was concluded that Lawsone has coordinated with Fe^{2+} through the phenolic oxygen, aromatic ring-OH and C=O group of the p-benzo quinine resulting in the formation of Fe^{2+} -Lawsone complex on the anodic sites of the metal surface.

In a related study carried out to investigated the inhibitive action of aqueous extract from henna leaves on Carbon steel in 1 M HCl solution by weight loss and potentio dynamic polarization techniques, the protective film and the mechanism of the inhibitor had been analyzed using FTIR and SEM respectively (Hamdy and Nour, 2012). For FT-IR studies, analytical FT-IR Perkin, instrument was used. The surface of the dried specimens was scratched and the resultant powder was used. The spectra of all studied samples were measured in the range of 400 to 4000 cm^{-1}. The main constituent of Henna extract, Lawsone was also determined. The phenolic –OH stretching appeared at 3440 cm^{-1}. The peaks formed at 2937 and 2092 cm^{-1} can be assigned to aliphatic and aromatic C-H. The aromatic C=C stretching frequency appeared at 1403 cm^{-1}. The C=O stretching frequency appeared at 1634

cm^{-1}. The FTIR spectrum of the protective film formed on the surface of the metal after immersion was found that, almost all the peaks observed for henna extract are also noticed for C-Steel immersed in 1 M HCl containing 3000 mg/L of henna extract. Phenolic –OH stretching has shifted from 3440 to 3385 cm^{-1}. The aromatic C=C stretching shifted from 1403 to 1407 cm^{-1}. The C=O stretching frequency has been shifted from 1634 to 1629 cm^{-1} indicates formation of Iron-Plant extract complex or salt. The phenol group of lawsone would donate electron to the metal to achieve its noble state of orbit, while the metal would received the electron to become more stable. Thus, indirectly retard further redox reaction and could prevent metal from corrosion attack.

Surface morphological examination of C-steel specimens after immersions for 48 hrs in the acid solution containing optimum concentration of inhibitor and without inhibitor was carried out using JEOL-model JSM-53000 scanning electron microscopy (SEM).The SEM images were taken in and the study reveals that in the absence of plant extract, the C-steel surface was highly damaged with pitted areas. The shape is typical to pitting corrosion. In the presence of the inhibitor, SEM image shows a smooth surface with deposited extract on it for the specimen after immersion in 1 M HCl solution containing 3000 mg/L henna extract. By comparison of SEM images at the same magnifications, it was indicated that the pits disappear and C-steel is almost free from corrosion in HCl with plant extract solution. This is because of the formation of an adsorbed film of plant extracts inhibit pitting corrosion of C-steel in 1 M HCl solution (Rajendran et al, 2009: Hamdy and Nour, 2012).

CHAPTER THREE

3.0 MATERIALS AND METHOD

3.1 MATERIALS

Normal laboratory glass wares, Thermostat: manufactured by Shermond model number 258 and made in England, Gallenhamb Water bath: made in England manufactured by Medical instrument MFG. CO. Number 400013, Electronic weighing balance: manufactured by Wincom Mettler Toledo with model number SHP 0200413110 made in China, Tin: Analytical grade, 99.5% purity, BDH, Thermometer, FTIR Spectrometer: manufactured by Agilent technologies with model number Cary 630, Sodium Hydroxide: AR, 96.0% purity with maximum limit of impurities 0.01% U.N.No. 1282 made in china, Desiccators, Hydrochloric Acid: AR, 36%, Relative molecular mass 36.5, density 1.17g/cm^3 with maximum limit of impurities 0.0005% model No. 51500 made in China, Caffeine : BDH company made in England, Mortal and Pestle, Sieve, Henna leaves, Deionised water, Ethanol and Acetone.

3.2 METHODS

All the reagents used in this research were of analytical grade and deionised water was used for their preparation. The glass wares were washed with water and detergent, rinsed with deionised water and then soaked in absolute ethanol. A previously treated and weighed coupon was separately and completely immersed in a 100ml beaker containing the test solution at a specific concentration with and without the inhibitor. The beaker was inserted into a thermostatic water bath maintained at a particular temperature. The coupon was withdrawn from the test solution at intervals of time, it was then washed with deionised water and light brush, dried in acetone and reweighed. The difference in weight was taken as the weight loss (Youssoufi *et al.,* 2013). All experiments were conducted in triplicate and the average weight losses were taken and recorded to minimise random error in all the procedures.

3.2.1 Coupon Preparation

The tin sheet used for the study is obtained from Metal Focus Fabrication Technology Incubation Centre complex, Farm Centre Kano State, Nigeria. The sheet was mechanically pressed-cut into coupons, each of dimensions 2.0 cm × 2.0 cm × 0.001 cm containing a small hole drilled near the upper edge. Each coupon was degreased by washing with ethanol, dipped in acetone and allowed to dry in air before they were preserved in a desiccator (Breket and Yurt, 2001).

3.2.2 Coupon Density Determination

The volume of the tin sheet sample was measured by the method of displacement of water by the metal. To find the volume, a graduated cylinder was filled with water and the initial volume was recorded. Then the metal sample was carefully dropped into the graduated cylinder and the new volume was also recorded. The difference between the two volumes gives the volume of the tin sheet sample (Ibrahim, 2007). Hence, the density g/cm^3 of the metal was determined by dividing its mass by the obtained volume.

3.2.3 Sample Collection

Fresh leaves of the henna plant were obtained from a garden at Tudun Yola, Gwale Local Government Kano State and was identified at the Plant Science Department of Bayero University, Kano with Herbarium Accession Number BUKHAN 0379 (Appendix 3). The leaves were then washed with deionised water after collection and air dried. The leaves were ground into fine powder form and were sieved to pass through a 250 nm meshed sieve. (Anozie *et al,* 2011).

3.2.4 Preparation of 1000mg/L Henna in 1M Hydrochloric acid:

The solution was prepared by weighing 1.0g of the henna powder in to 1000ml volumetric flask containing 1.0 M Hydrochloric acid solution, made up to the mark with test solution, shake to dissolved and left to stand for 24 hours. This represent the stock solution of the inhibitor (1000mg/L) from which various concentrations of 10, 20, 30, 40 and 50 mg/L were prepared by serial dilution. Similar procedure was repeated with 1M sodium hydroxide solution *(*Nnanna*, et al* 2010).

3.2.5 Preparation of 1000mg/L Caffeine in 1M Hydrochloric acid

Caffeine ($C_8H_{10}N_4O_2$) was prepared in similar manner as described for henna.

3.2.6 Preparation of Corrodent Concentrations

The corrodents solutions were prepared for different concentrations of 0.2, 0.4, o.6, 0.8 and 1.0M HCl and NaOH respectively (Muhammad *et al.,* 2014). The concentration of the stock acid was calculated using the formula: M = 10% purity d/Mr where, M is the molarity, d is the density and Mr is the relative molecular mass. From which certain volumes of the stock acid were measured into the 1000cm^3 volumetric flask contained deionised water and made up to the mark with the deionised water to give the new concentration required by serial dilution method (Nnanna *et al*., 2011a).

40.0g of sodium hydroxide pellet was weighed in a 500cm^3 beaker and then dissolved the solid with deionized water. The mixture was transferred quantitatively to the 1000cm^3 volumetric flask and made up to the mark with deionised water. This is 1.0 M NaOH solution from which different concentrations of 0.2, 0.4, 0.6 and 0.8 M was prepared by serial dilution (Nnanna *et al*., 2011b).

3.2.7 Effect of Immersion Time

To study the effect of the immersion time, the procedure reported by Ituen *et al.,* (2013) and Ogoko *et al*, (2009) was adopted. A Previously weighed tin coupon was separately and completely immersed in 100ml of 0.2M hydrochloric acid solution in an open beaker using Mettler Toledo electronic weighing balance. The beaker was immersed into a water bath maintained at 298K. Each coupon was withdrawn from the test solution washed with deionised water and dried with acetone after immersion time of 5mins, 10mins, 15mins, 30mins, 45mins, 1hr, 2hours 3hours, 4hours, 5hours, 6hours, 12hours and 24hours respectively. The weight difference of the metal before and after immersion was recorded as weight loss due to corrosion. This procedure was repeated for 0.2M sodium hydroxide solution.

3.2.8 Effect of Corrodent Concentration

Fresh samples of coupons were separately immersed in beakers containing 0.2M, 0.4M, 0.6M, 0.8M and 1M Solutions of hydrochloric acid and each beaker immersed in water bath maintained at 298K for 3 hours. The weight difference before and after immersion was recorded as weight loss due to corrosion. This procedure was repeated for sodium hydroxide at 298K and 4 hours to test effect of increase in concentration of corrodent (Omotoyinbo *et al.*, 2013).

3.2.9 Effect of Temperature

Weight loss of tin coupons was tested in 1M hydrochloric acid at 298K, 303K, 308K, 313K, 318K and 323K for 3 hours. This procedure was repeated for 1M sodium hydroxide for 4 hours to test the effect of increase in the temperature of corrodent solutions (James and Akaranta, 2009: Labjar *etal*, 2011).

3.2.10 Effect of Inhibitor Concentration

Weight loss of tin coupon was tested in 10, 20, 30, 40 and 50 mg/L of the inhibitors in 1M hydrochloric acid solution at 323K and 303 K for 3 hours. This procedure was repeated for the same inhibitor concentrations in 1M sodium hydroxide at 323K and 303 K for 4 hours to test the efficiency of Henna and Caffeine powders as inhibitors (El-Etre, 2001: Gao and Liang, 2007).

3.2.11 Infra-red Analysis

FTIR Instrument of model: Cary 630 FTIR Spectrometer (Agilent Technologies) was used to identify the major functional groups present in both *Lawsonia inermis* leaves and caffeine powder. Same instrumentation was used for the corrosion product of the Tin coupons with and without the inhibitors (Gowri *et al.,* 2012). Attenuated total reflection (ATR) technique was employed to measured the sample directly into the agilent technology spectrometer which does not required any sample preparation before measurement were made (Pinkerneil *et al*., 2012).

3.3 PROCEDURE FOR THE KINETIC STUDY

The first and second order equations are applied to model the kinetics of the corrosion process of tin for varied time of immersion periods (1-24 hrs) in acidic and alkaline solutions without inhibitor at minimum concentration and temperature of 0.2 M and at 298 K respectively. Equations 15, 16 and 17 were used in the investigation and approximation of the reaction order, rate constant and half-life.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 RESULTS

4.1.1 Effect of Immersion Time without Inhibitor

Weight loss of tin metals in 0.2 M HCl and NaOH solutions at 298K and Various time of immersion period were determined and the results were as presented in Fig. 4.1.

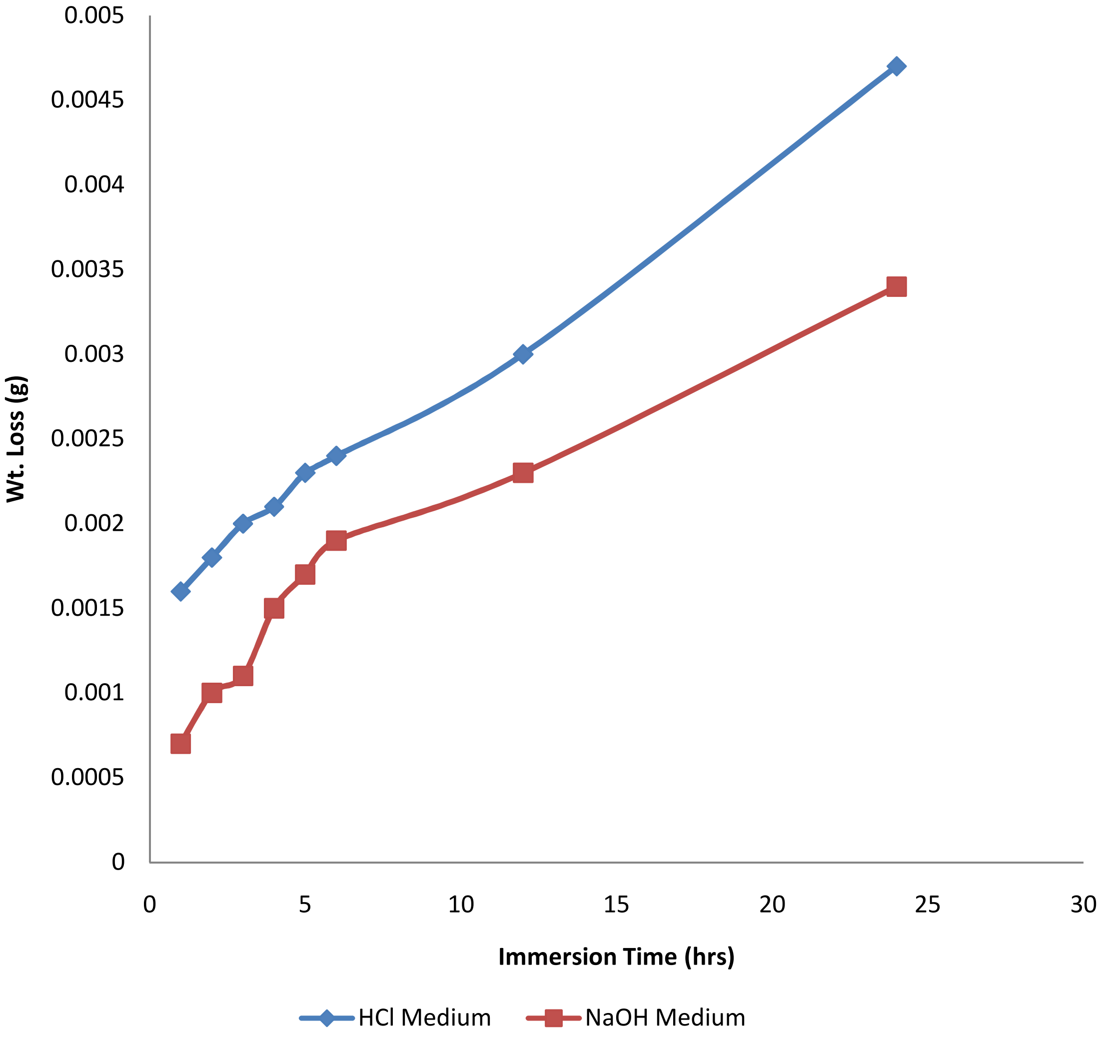


Figure 4.1: Variation of Weight loss with Time of Exposure in 0.2M HCl and NaOH Solutions without Inhibitor at Room Temperature

4.1.2 Effect of Corrodent Concentration

A plot of weight loss variation with corrodent concentration for the corrosion of tin coupon in varying concentration of HCl and NaOH solutions for 3 h and 4 h respectively without the inhibitor at 298K is as presented in Fig. 4.2.

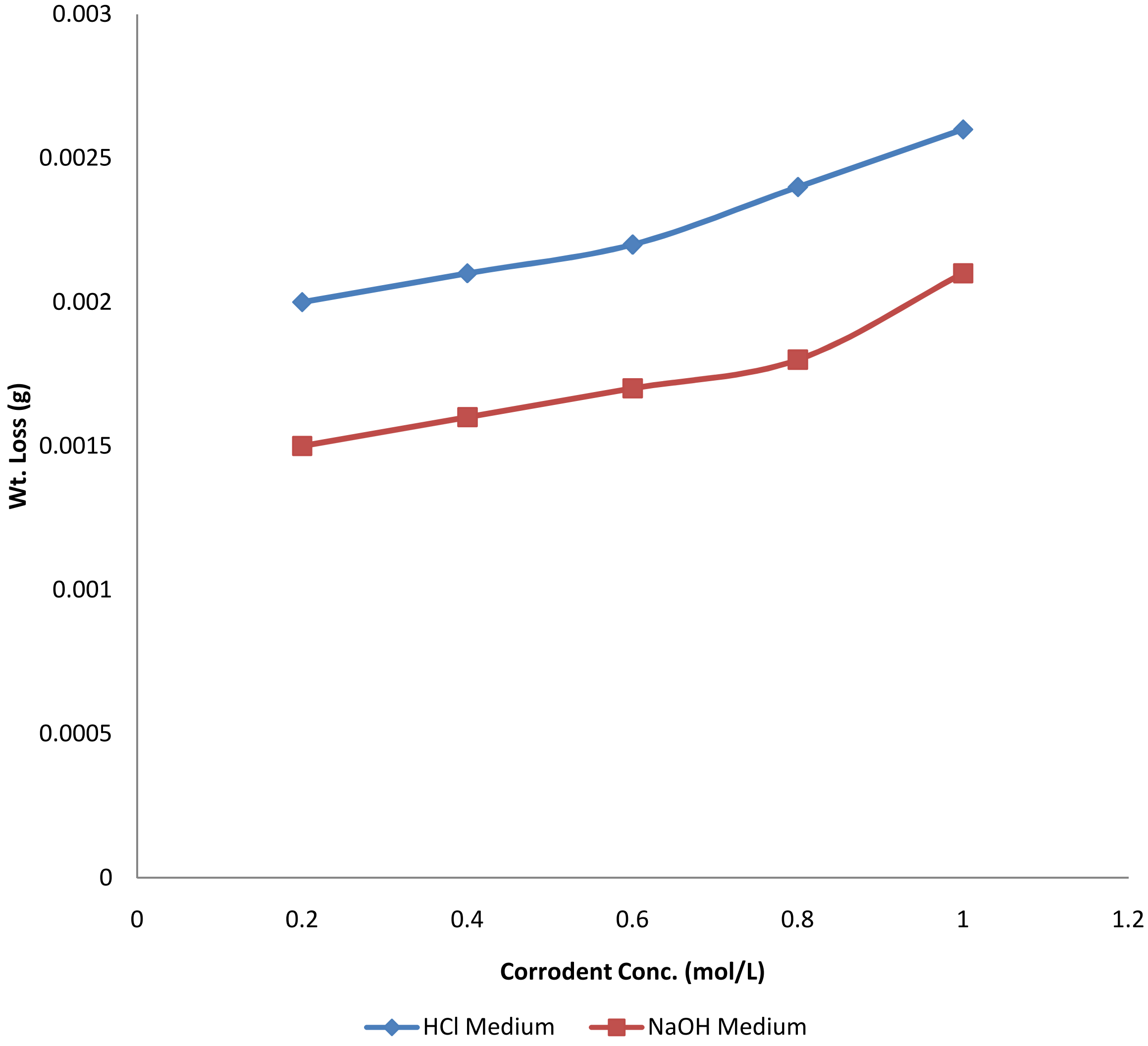


Figure 4.2: Variation of Weight loss with Concentration of HCl and NaOH for 3hrs and 4hrs respectively at 298 K.

4.1.3 Effect of Temperature on the Corrodent Concentration

Weight loss experiment was conducted to test for effect of change in the temperature of the corrodent both in 1 M HCl and 1 M NaOH solution at 298K for 3 hrs and 4 hrs respectively from the range 298, 303, 308, 313, 318 and 323 K. The result is presented in Fig. 4.3.

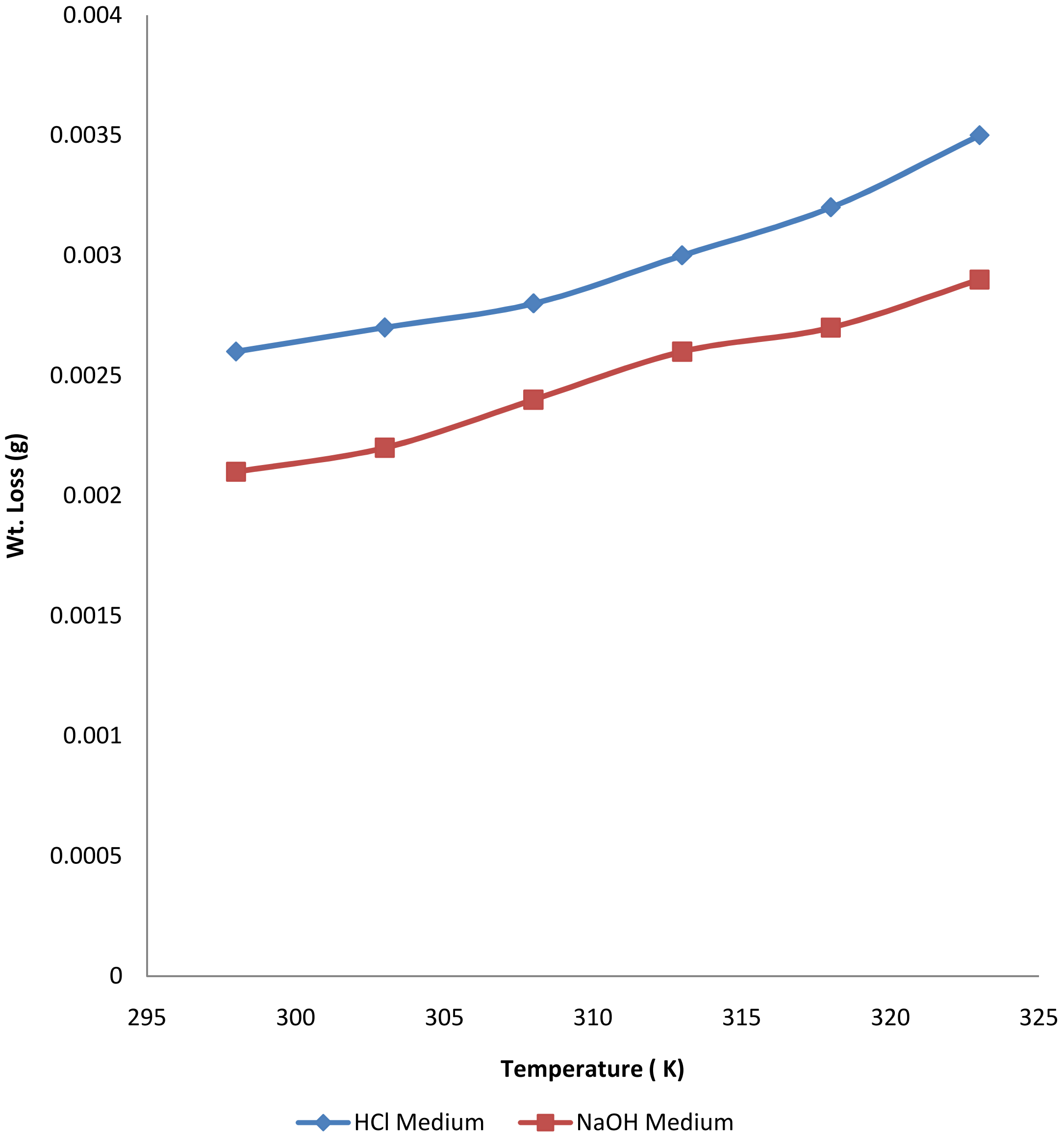


Figure 4.3: Variation of Weight loss with Temperature in 1.0M Corrodent Concentrations at a Fixed Time of Exposure without Inhibitor.

4.1.4 Effect of Inhibitors on the Corrosion of Tin Metal

Weight loss of tin metals were carried out to see the effect of increase in concentration of the inhibitors (10, 20, 30, 40 and 50 mg/L) in 1 M HCl and 1 M NaOH solutions at 323 K for 3 hours and 4 hours respectively. The weight loss results obtained with increase in concentration is as presented in Fig. 4.4 and the inhibition efficiency is presented as in Fig.4.5. While Table 4.1- 4.5 showed the comparison of weight loss, corrosion rate in the absence and presence of inhibitors, inhibition efficiency, surface coverage and increased in concentrations of the inhibitors.

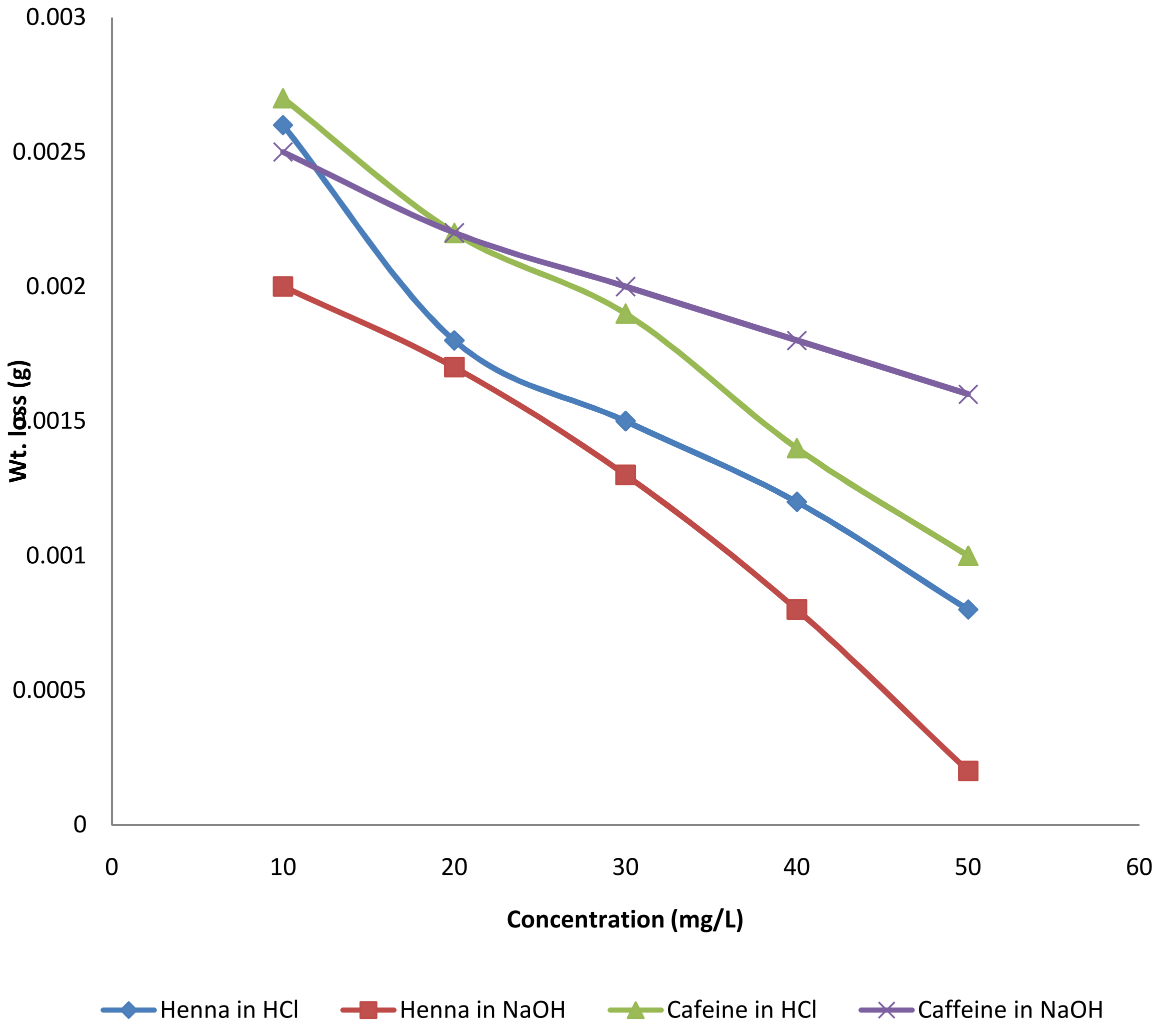


Figure 4.4: Variation of Weight loss with Concentrations of *Lawsonia innermis,* and Caffeine in 1.0M HCl and 1.0 M NaOH Solutions at 323K for 3 and 4 hours respectively.

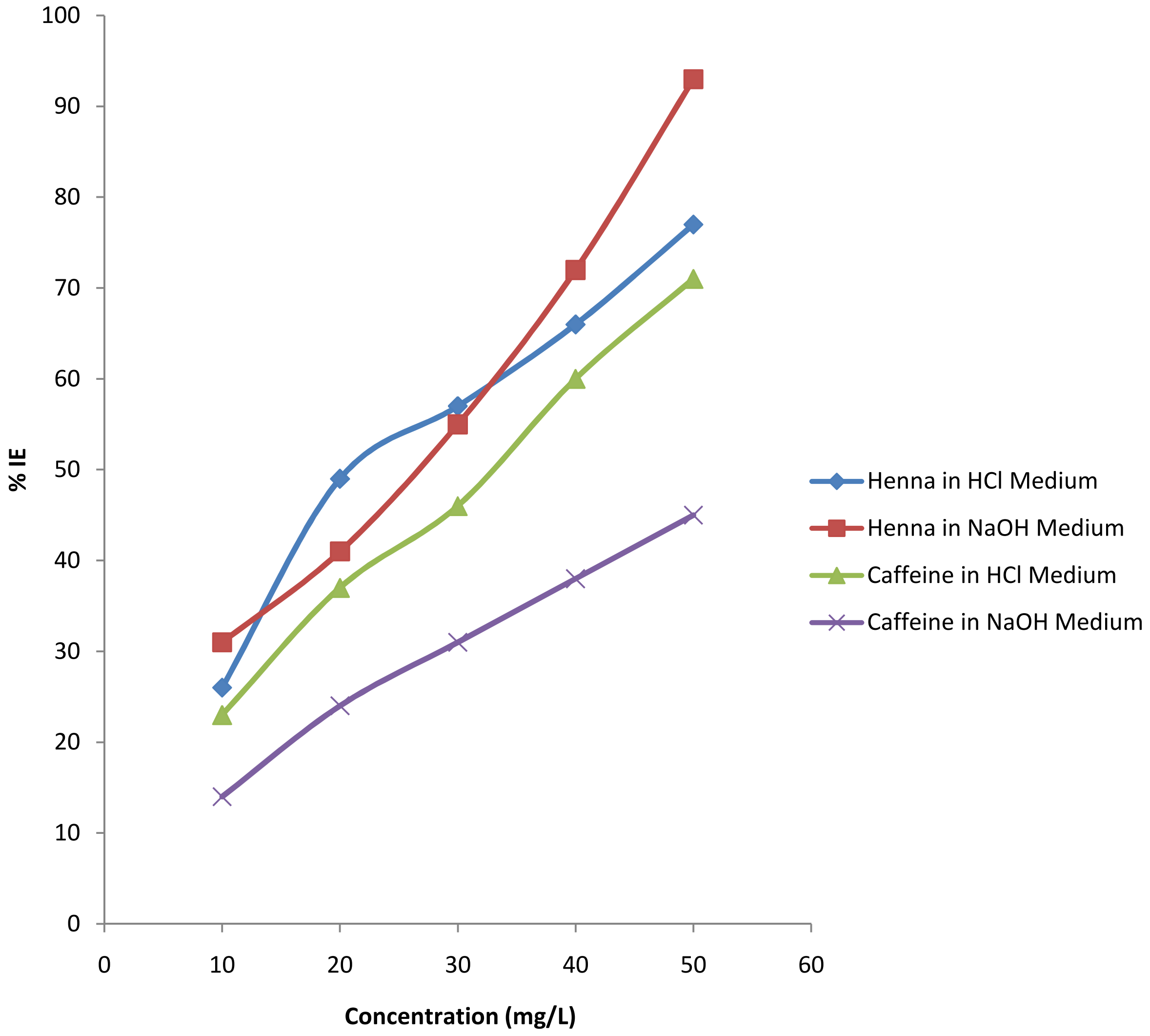


Figure 4.5: Variation of Inhibition Efficiency (%I.E) with Various Concentrations of Inhibitors in Acidic and Alkaline Media Contained *Lawsonia innermis, L*. and Caffeine at 323K

Table 4.1: Corrosion Rate in the Absence of Inhibitor

Temperature (K)	**Acid**		**Alkaline**	
	$\Delta w(mg)$	**C.R (mm/y)**	$\Delta w(mg)$	**C.R (mm/y)**
298	2.6000	37960	2.1000	22995
303	2.7000	39420	2.2000	24090
308	2.8000	40880	2.4000	26280
313	3.0000	43800	2.6000	28470
318	3.2000	46720	2.7000	29565
323	3.5000	51100	2.9000	31755

Table 4.2: Weight loss, Degree of Surface Coverage (DSC), Inhibition Efficiency (IE) and Corrosion rate (CR) for varied concentration of Caffeine in 1.0 M HCl and 1.0 M NaOH Solutions for 3hrs and 4hrs respectively at 323K

INH. Conc. (mg/L)	**ACIDIC MEDIUM**				**BASIC MEDIUM**			
	Wt. loss (g)	DSC (θ)	IE (%IE)	CR (mm/y)	Wt. loss (g)	DSC (θ)	IE (% IE)	CR (mm/y)
10	0.0027	0.2286	22.86	39420	0.0025	0.1379	13.79	27375
20	0.0022	0.3714	37.14	32120	0.0022	0.2414	24.14	24090
30	0.0019	0.4571	45.71	27740	0.0020	0.3103	31.03	21900
40	0.0014	0.6000	60.00	20440	0.0018	0.3793	37.93	19710
50	0.0010	0.7143	71.43	14600	0.0016	0.4483	44.83	17520

Table 4.3: Weight loss, Degree of Surface Coverage (DSC), Inhibition Efficiency (IE) and Corrosion rate (CR) for Varied concentration of Henna extract in 1.0 M HCl and 1.0 M NaOH Solutions for 3hrs and 4hrs respectively at 323K

INH. Conc. (mg/L)	**ACIDIC MEDIUM**				**BASIC MEDIUM**			
	Wt. loss (g)	DSC (θ)	IE (%IE)	CR (mm/y)	Wt. loss (g)	DSC (θ)	IE (% IE)	CR (mm/y)
10	0.0026	0.2571	25.71	37960	0.0020	0.3103	31.03	21900
20	0.0018	0.4857	48.57	26280	0.0017	0.4138	41.38	18615
30	0.0015	0.5714	57.14	21900	0.0013	0.5517	55.17	14235
40	0.0012	0.6571	65.71	17520	0.0008	0.7241	72.41	8760
50	0.0008	0.7714	77.14	11680	0.0002	0.9310	93.10	2190

Table 4.4: Weight loss, Degree of Surface Coverage (DSC), Inhibition Efficiency (IE) and Corrosion rate (CR) for varied concentration of Caffeine in 1.0 M HCl and 1.0 M NaOH Solutions for 3hrs and 4hrs respectively at 303K

INH. Conc. (mg/L)	**ACIDIC MEDIUM**				**BASIC MEDIUM**			
	Wt. loss (g)	DSC (θ)	IE (%IE)	CR (mm/y)	Wt. loss (g)	DSC (θ)	IE (% IE)	CR (mm/y)
10	0.0019	0.2963	29.63	27740	0.0017	0.2273	22.73	18615
20	0.0014	0.4815	48.15	20440	0.0015	0.3182	31.82	16425
30	0.0012	0.5556	55.56	17520	0.0014	0.3636	36.36	15330
40	0.0009	0.6667	66.67	13140	0.0012	0.4545	45.45	13140
50	0.0006	0.7778	77.78	8760	0.0010	0.5455	54.55	10950

Table 4.5: Weight loss, Degree of Surface Coverage (DSC), Inhibition Efficiency (IE) and Corrosion rate (CR) for varied concentration of Henna extract in 1.0 M HCl and 1.0 M NaOH Solutions for 3hrs and 4hrs respectively at 303K

INH. Conc. (mg/L)	**ACIDIC MEDIUM**				**BASIC MEDIUM**			
	Wt. loss (g)	DSC (θ)	IE (%IE)	CR (mm/y)	Wt. loss (g)	DSC (θ)	IE (% IE)	CR (mm/y)
10	0.0013	0.5185	51.90	18980	0.0011	0.5000	50.00	12045
20	0.0011	0.5926	59.26	16060	0.0009	0.5909	59.09	9855
30	0.0009	0.6667	66.67	13140	0.0005	0.7727	77.27	5475
40	0.007	0.7407	74.07	10220	0.0003	0.8640	86.40	329
50	0.0004	0.8519	85.19	5840	0.0001	0.9545	95.45	110

4.1.5 Adsorption Consideration

The adsorption behaviour of *Lawsonia inermis,L (Henna)* and caffeine were studied by fitting data obtained from degree of surface coverage to different adsorption isotherms including Langmuir, Temkin, Frumkin, Flory-Huggins El-Awady, and Freundlich adsorption isotherms as presented in Table 4.6 using equations 22-27.

Table 4.6: Correlation coefficient (R^2) values for Adsorption Isotherms

Adsorption Isotherms	**Henna**		**Caffeine**	
	Acid	**Base**	**Acid**	**Base**
Langmuir	0.962	0.669	0.892	0.981
Temkin	0.988	0.876	0.946	0.978
Frumkin	0.913	0.990	0.968	0.973
Flory-Huggins	0.886	0.287	0.749	0.963
El-Awady	0.980	0.780	0.957	0.959
Freundlich	0.972	0.957	0.993	0.997

4.1.6 Thermodynamic Study

In order to study the effect of temperature on the corrosion of tin metal in 1.0M concentration of HCl and NaOH without inhibitor, the Arrhenius equation was used (Muhammad *et al.*, 2014). The calculated values for the activation energy, entropy and enthalpy of the system can be observed in Tables 4.7, 4.8, and 4.9 as well as the free energy of both uninhibited and inhibited process. The plot of the equations used for corrosion activation energy, entropy and enthalpy without the inhibitor are shown in Fig. 4.6 and Fig. 4.7 (Ituen *et al*., 2013).

Table 4.7: Calculated Values for Activation energy, Entropy, Enthalpy and Free energy of the uninhibited Corrosion System

Activation Energy (E_a)		**Entropy (ΔS)**		**Enthalpy (ΔH)**		**Free Energy (ΔG)**	
Acid	**Base**	**Acid**	**Base**	**Acid**	**Base**	**Acid**	**Base**
9405Jmol^{-1}	10562Jmol^{-1}	255Jmol^{-1}	255Jmol^{-1}	6826 Jmol^{-1}K^{-1}	7983 Jmol^{-1}K^{-1}	-75.539 kJmol^{-1}	-74.382 kJmol^{-1}

Table 4.8: Calculated Values for Activation energy of Inhibitor System

Henna in Acid	Henna in Base	Caffeine in Acid	Caffeine in Base
E_a ($Jmol^{-1}$)	E_a ($Jmol^{-1}$)	E_a ($Jmol^{-1}$)	E_a ($Jmol^{-1}$)
28131	29589	20738	19075

Table 4.9: Calculated Values of free energy of Adsorption Inhibitors with Respective Kads Value for each System

Lawsonia inermis **(Henna)**		**Caffeine**	
$\Delta G, Acid$	$\Delta G, base$	$\Delta G, Acd$	$\Delta G, bas$
-3.245kjmol^{-1}	-3.280 kjmol^{-1}	-2.488 kjmol^{-1}	-1.047 kjmol^{-1}
Equilibrium constant of adsorption values (K_{ads})			
0.0603	0.0611	0.0455	0.02661

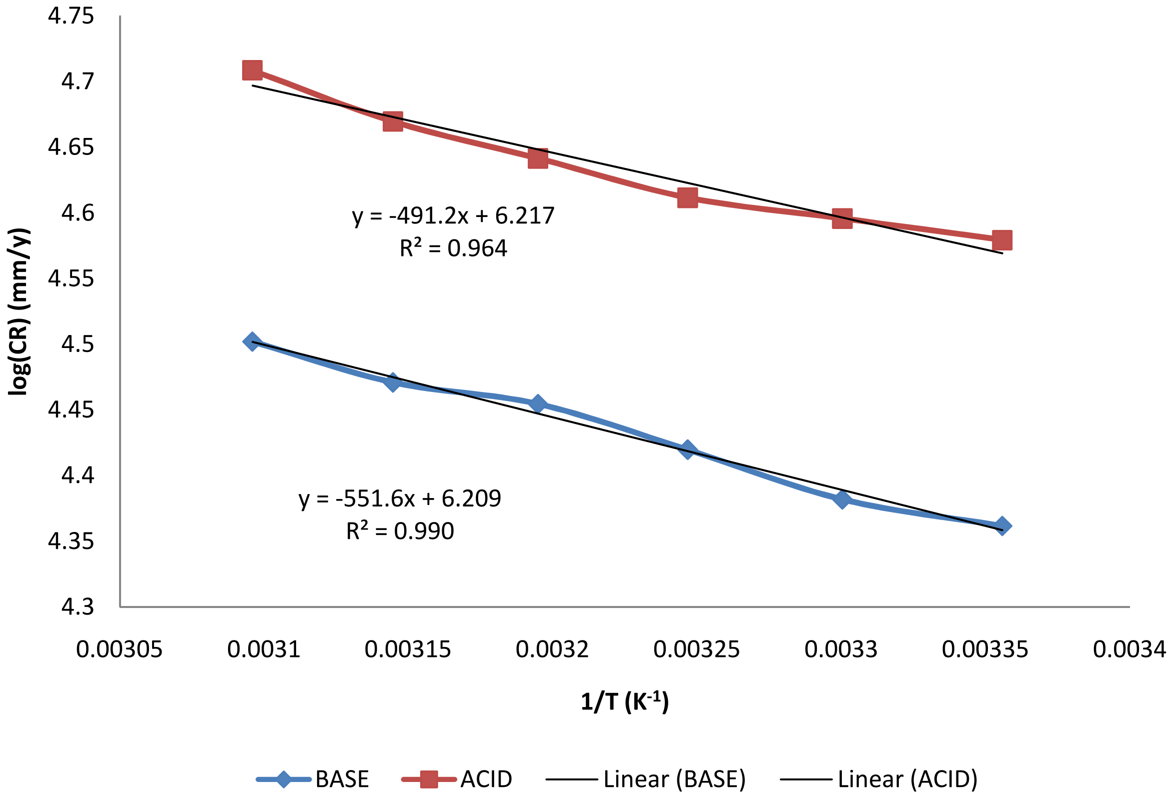


Figure 4.6: A Plot of log Corrosion rate (CR) Versus Temperature inverse in Acid and Base

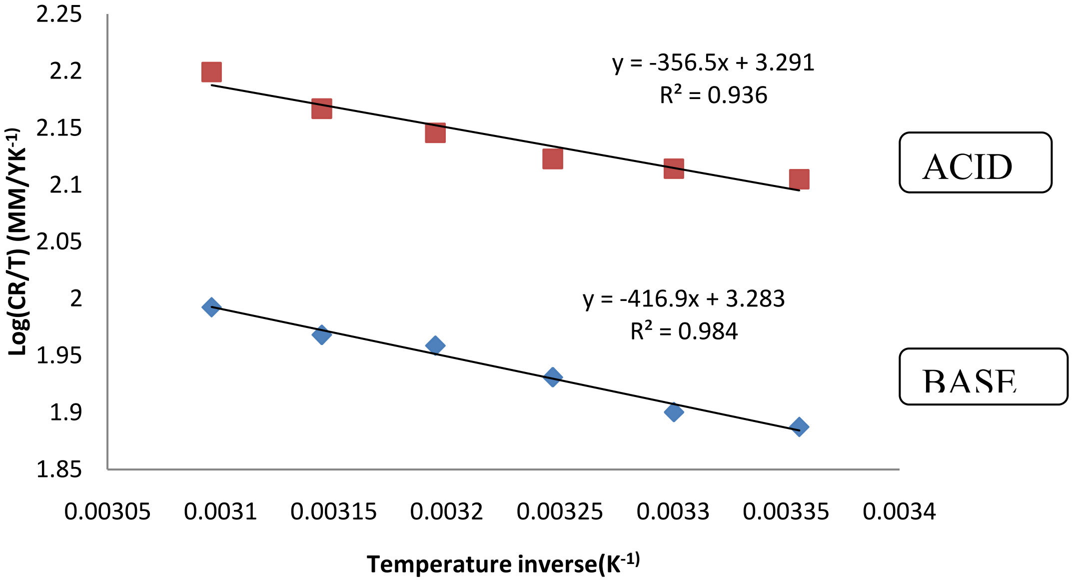


Figure 4.7: A Plot of log (CR/T) Versus Temperature inverse in Acid and Base

4.1.7 Kinetic Study

The plot of –log (weight loss) versus period of immersion gives high correlation value, $R^2 = 0.963$ in acid, obey the first order kinetic (see Fig. 4.8). Alternatively, A plot of weight loss inverse versus period of immersion gives high correlation value, $R^2 = 0.8736$ in alkaline medium and follow second order kinetic (Fig, 4.9).

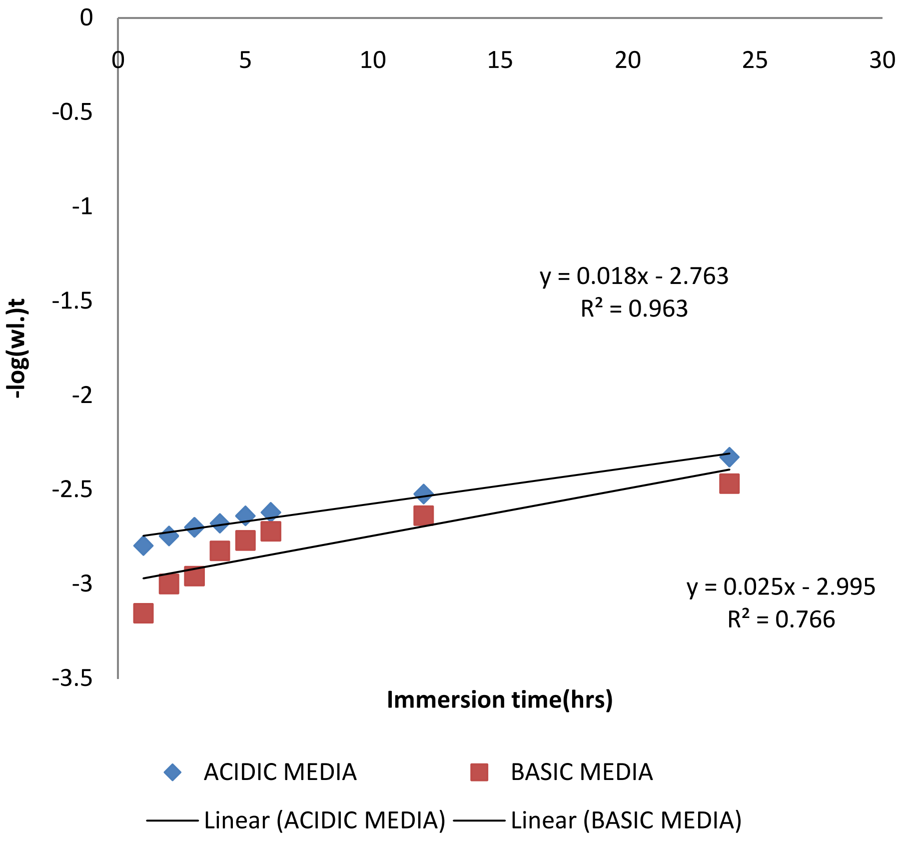


Figure 4.8: A Plot of –log of Weight loss Versus Various Time of Immersion in Acid and Alkaline

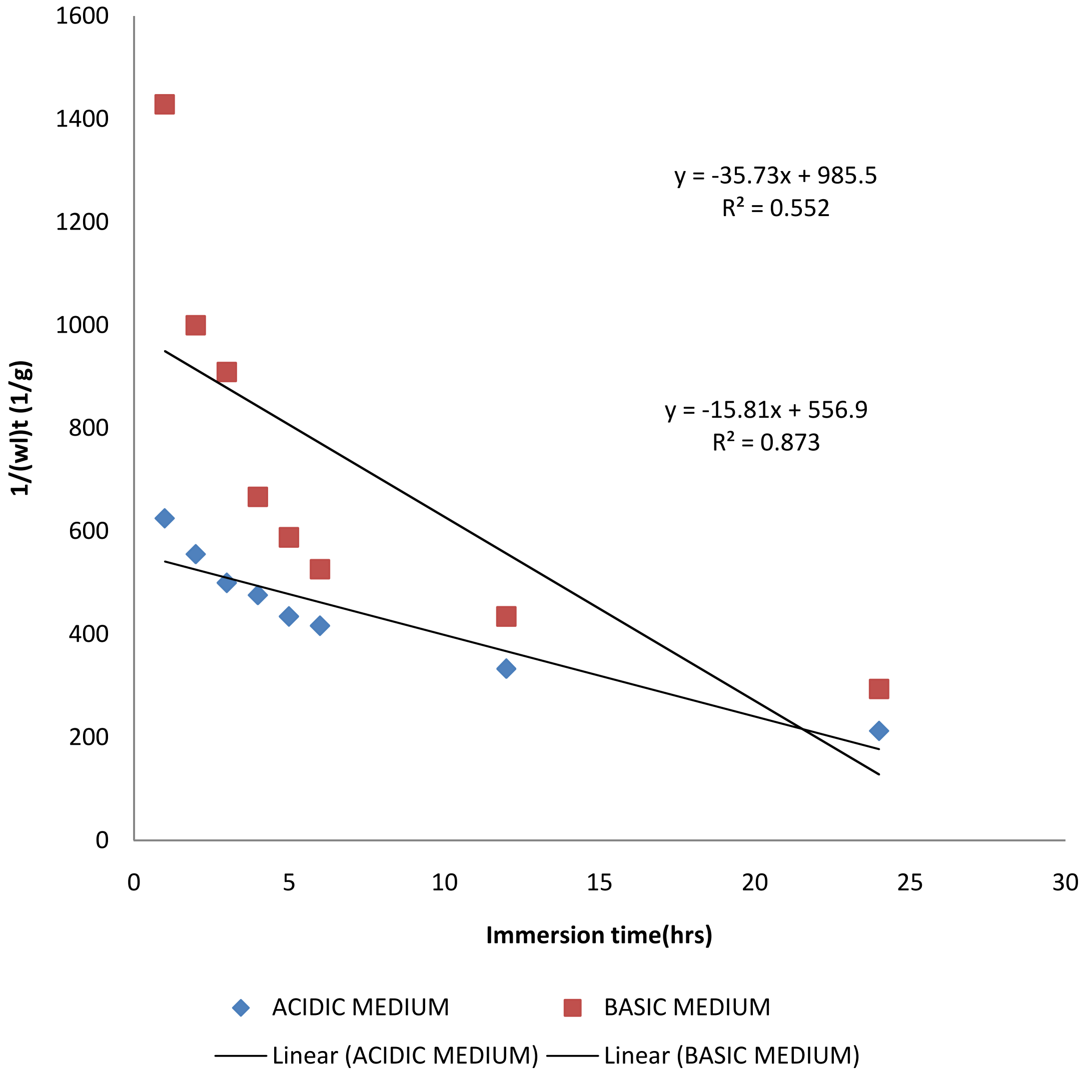
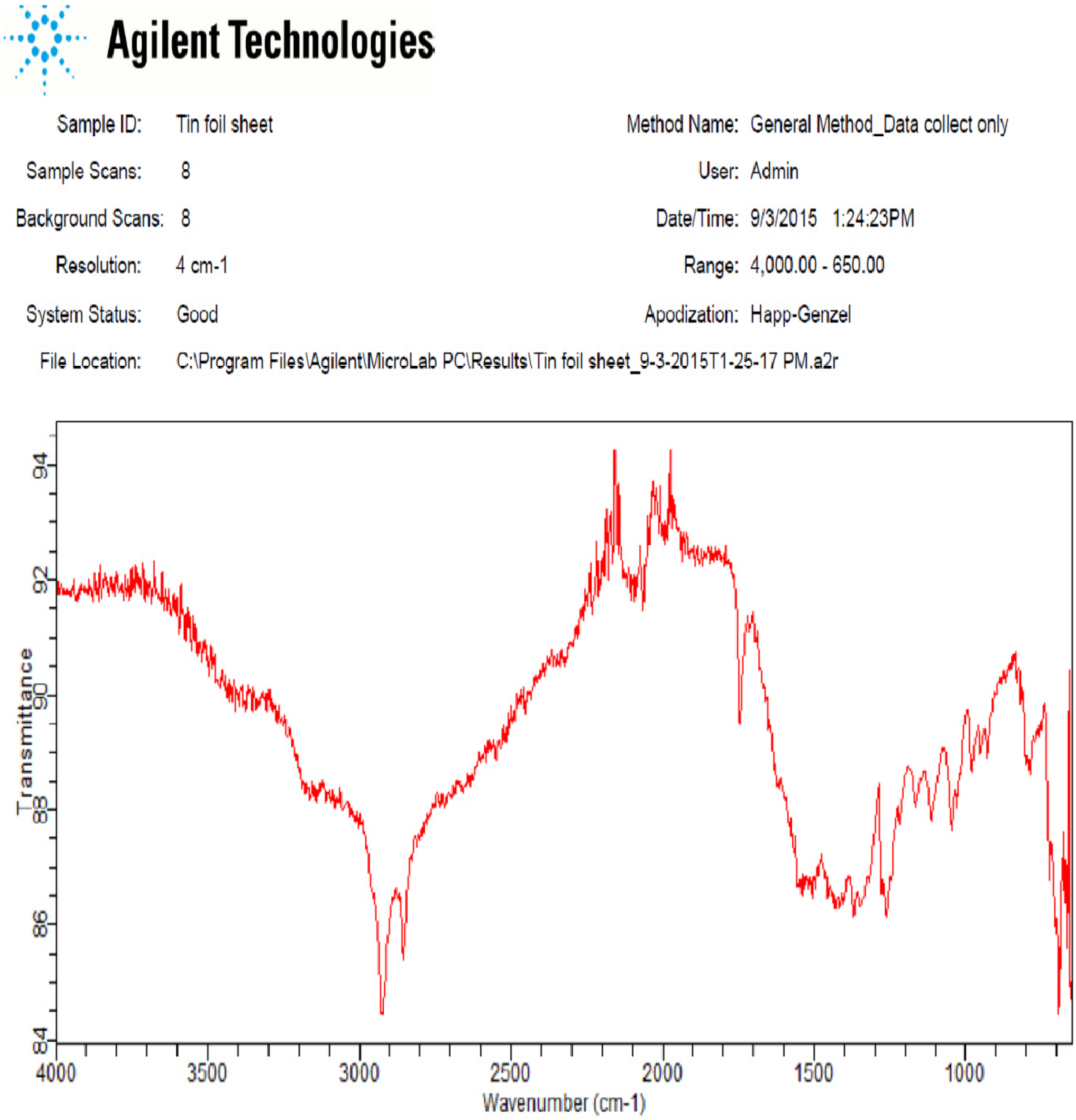


Figure. 4.9: A Plot of Weight loss Inverse Versus Time of Immersion in Acid and Alkaline

4.1.8 FTIR Consideration: Analysis of the Protective Film

The FTIR spectra has been determined and presented as they are shown in Figures 4.10 to 4.18 below:



Agilent Technologies

Sample ID: Tin foil sheet

Method Name: General Method_Data collect only

Sample Scans: 8

User: Admin

Background Scans: 8

Date/Time: 9/3/2015 1:24:23PM

Resolution: 4 cm-1

Range: 4,000.00 - 650.00

System Status: Good

Apodization: Happ-Genzel

File Location: C:\Program Files\Agilent\MicroLab PC\Results\Tin foil sheet_9-3-2015T1-25-17 PM.a2r

Figure 4.10: FTIR Absorbance Spectra of Pure Tin Sheet before Corroding

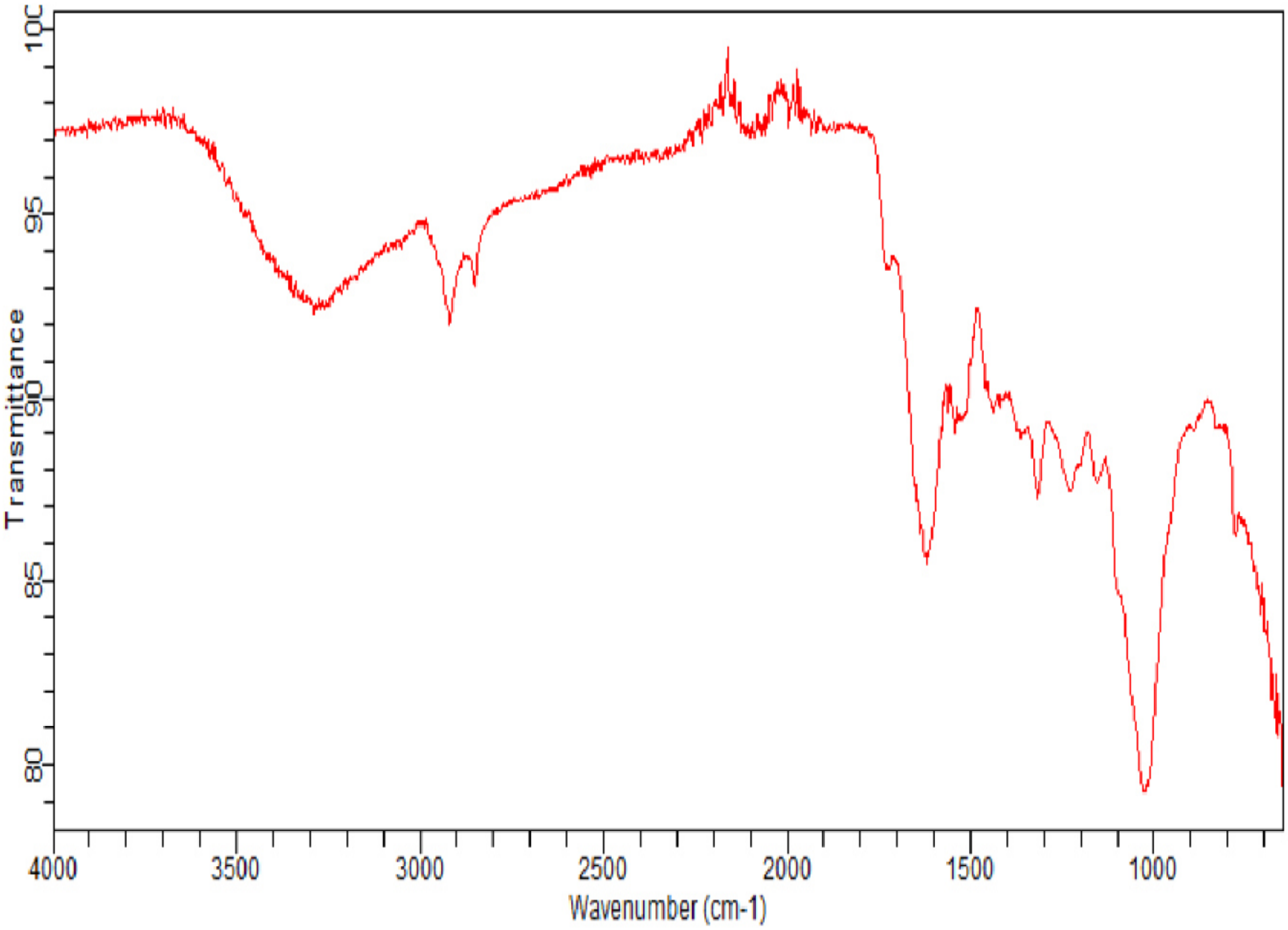


Figure 4.11: An FTIR Absorbance Spectrum of *Lawsonia inermis* Leaves Powder

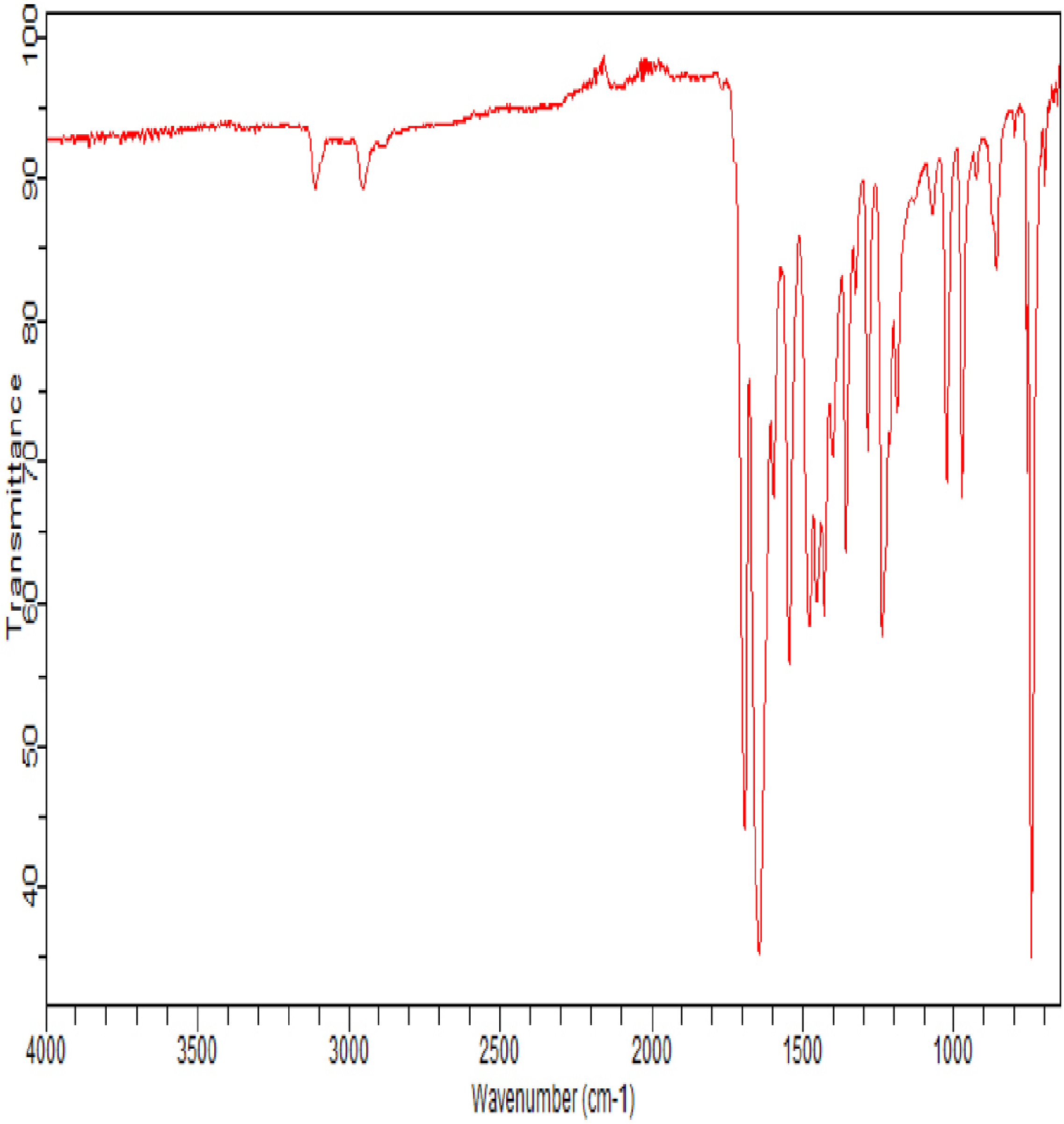


Figure 4.12: FTIR Absorbance Spectra of Solid Caffeine

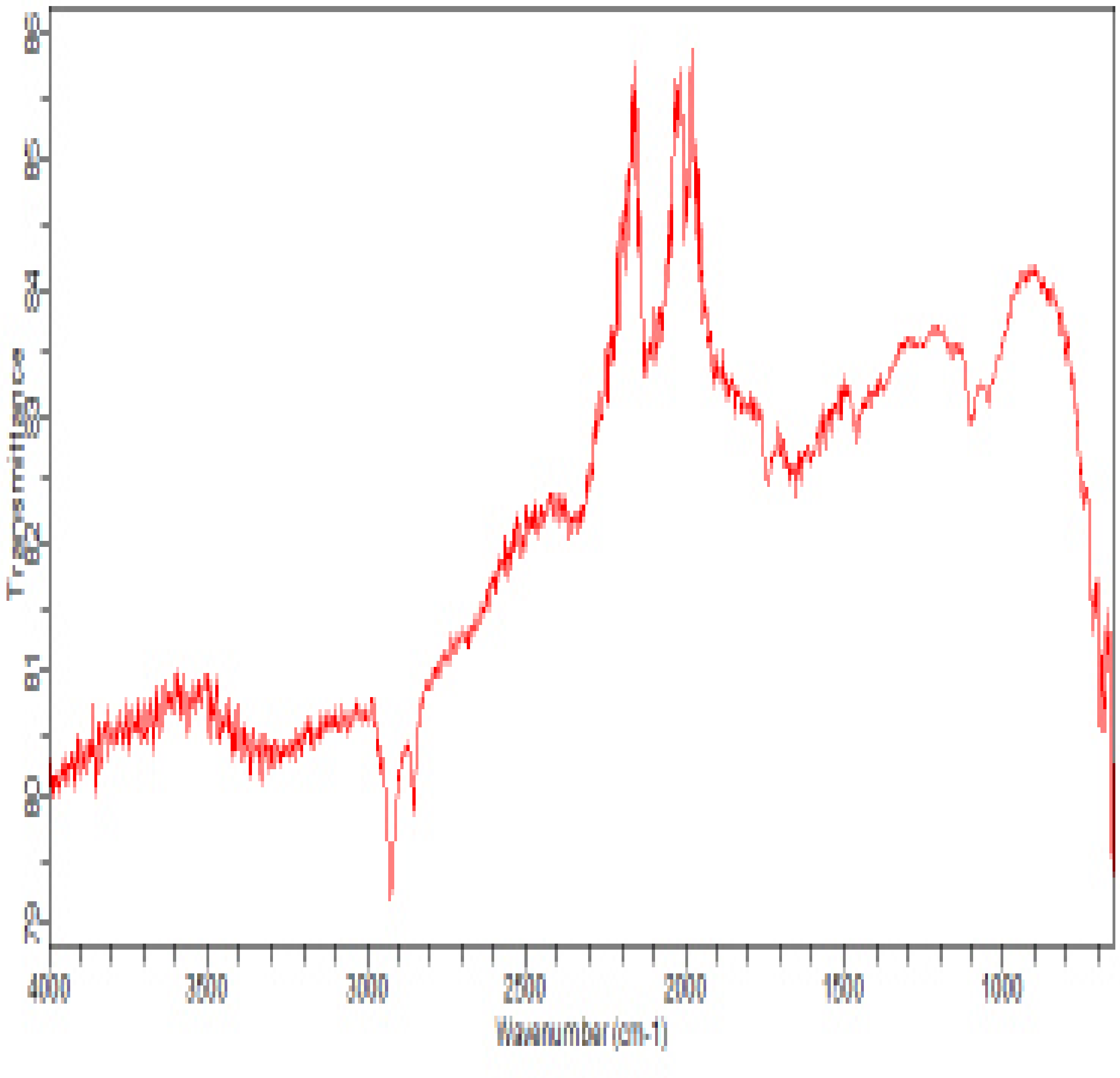


Figure 4.13: FTIR Absorbance Spectra of Tin Metal after Immersion in 1.0M HCl

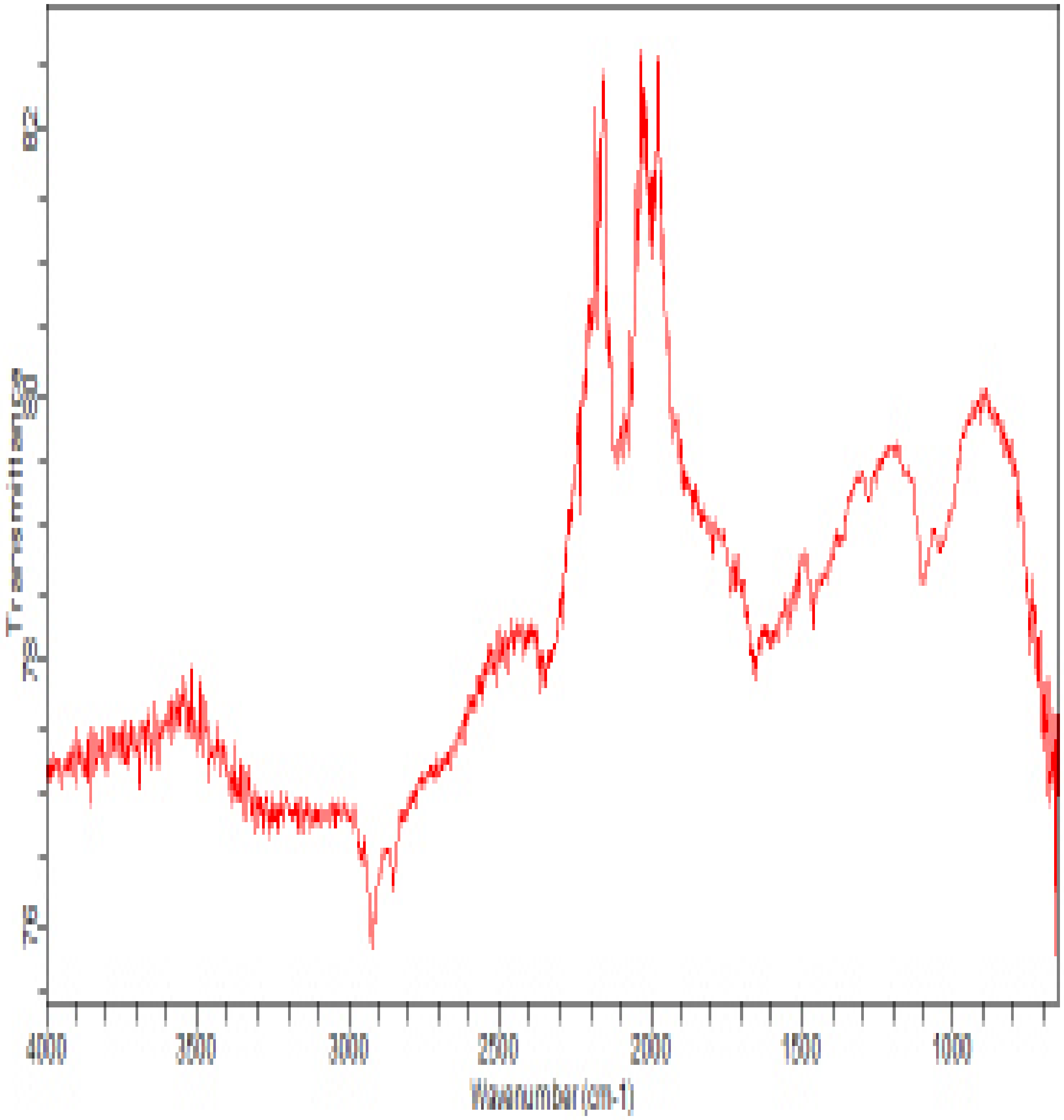


Figure 4.14: FTIR Absorbance Spectra of Tin Metal after Immersion in 1.0M NaOH

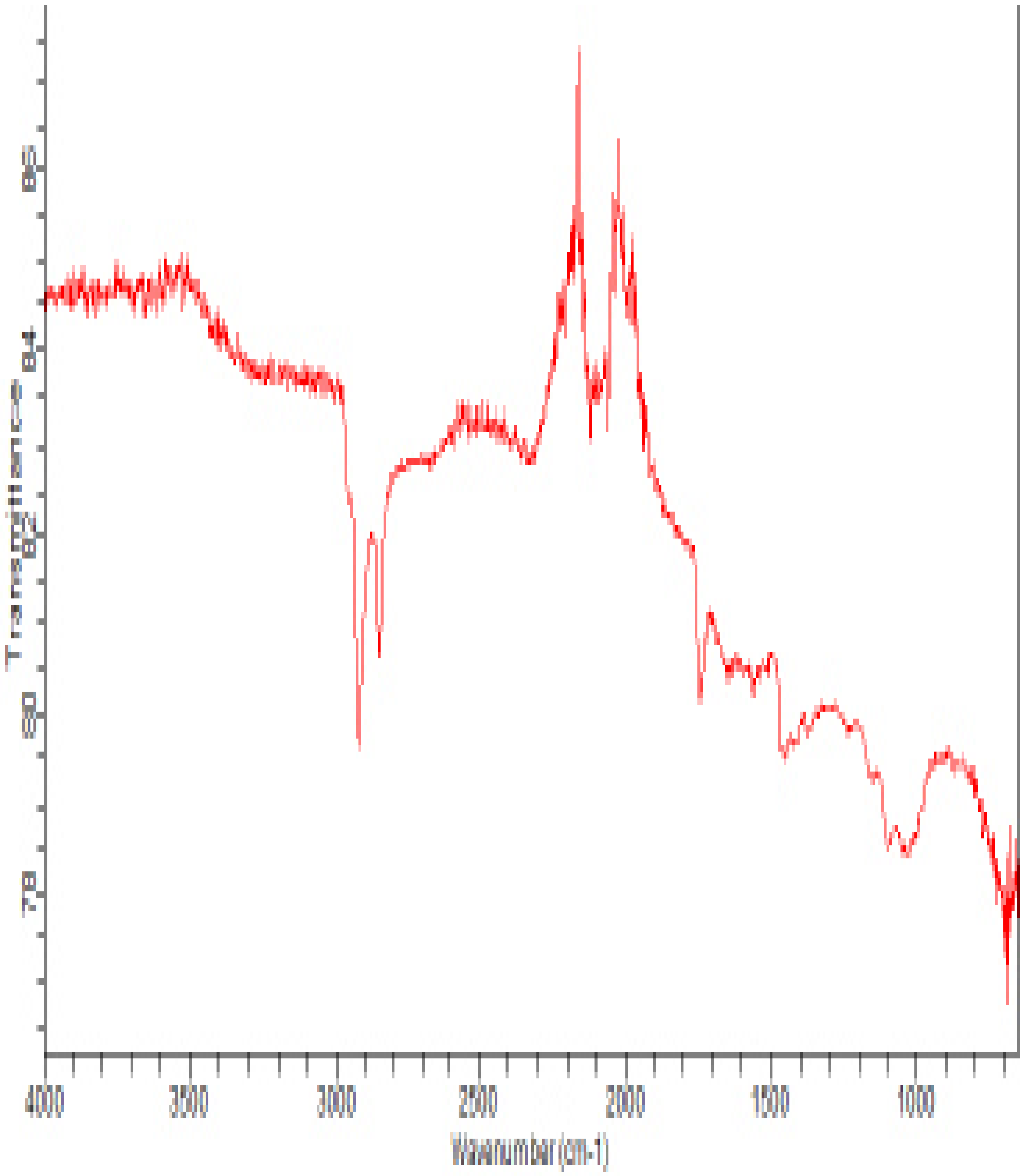


Figure 4.15: FTIR: Absorbance Spectra of Tin Metal in 1.0M HCl with Caffeine

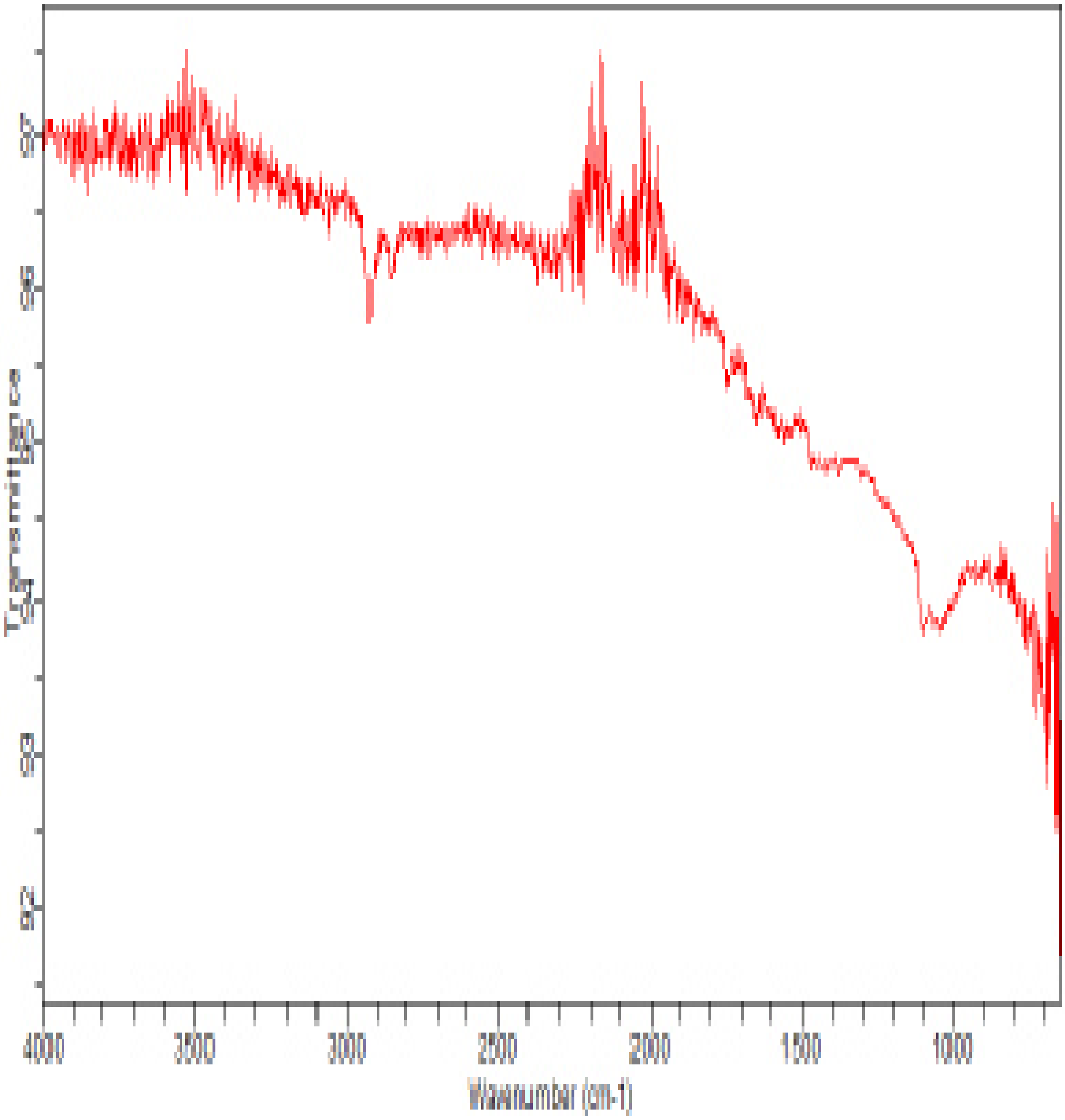


Figure 4.16: FTIR Absorbance Spectra of Tin Metal in 1.0M NaOH with Caffeine

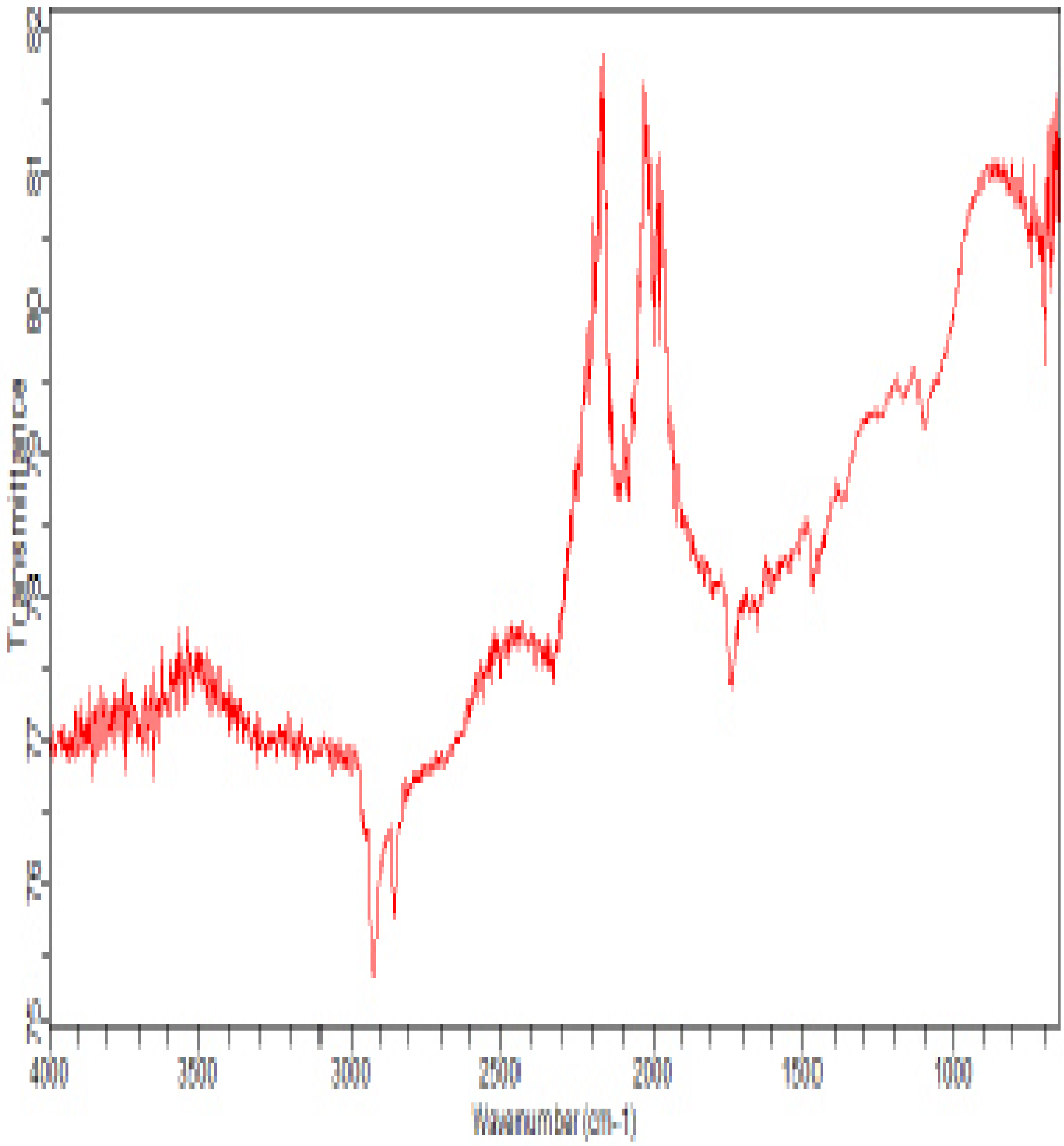


Figure 4.17: FTIR Absorbance Spectra of Tin Metal in 1.0M HCl with *Lawsonia inermis*

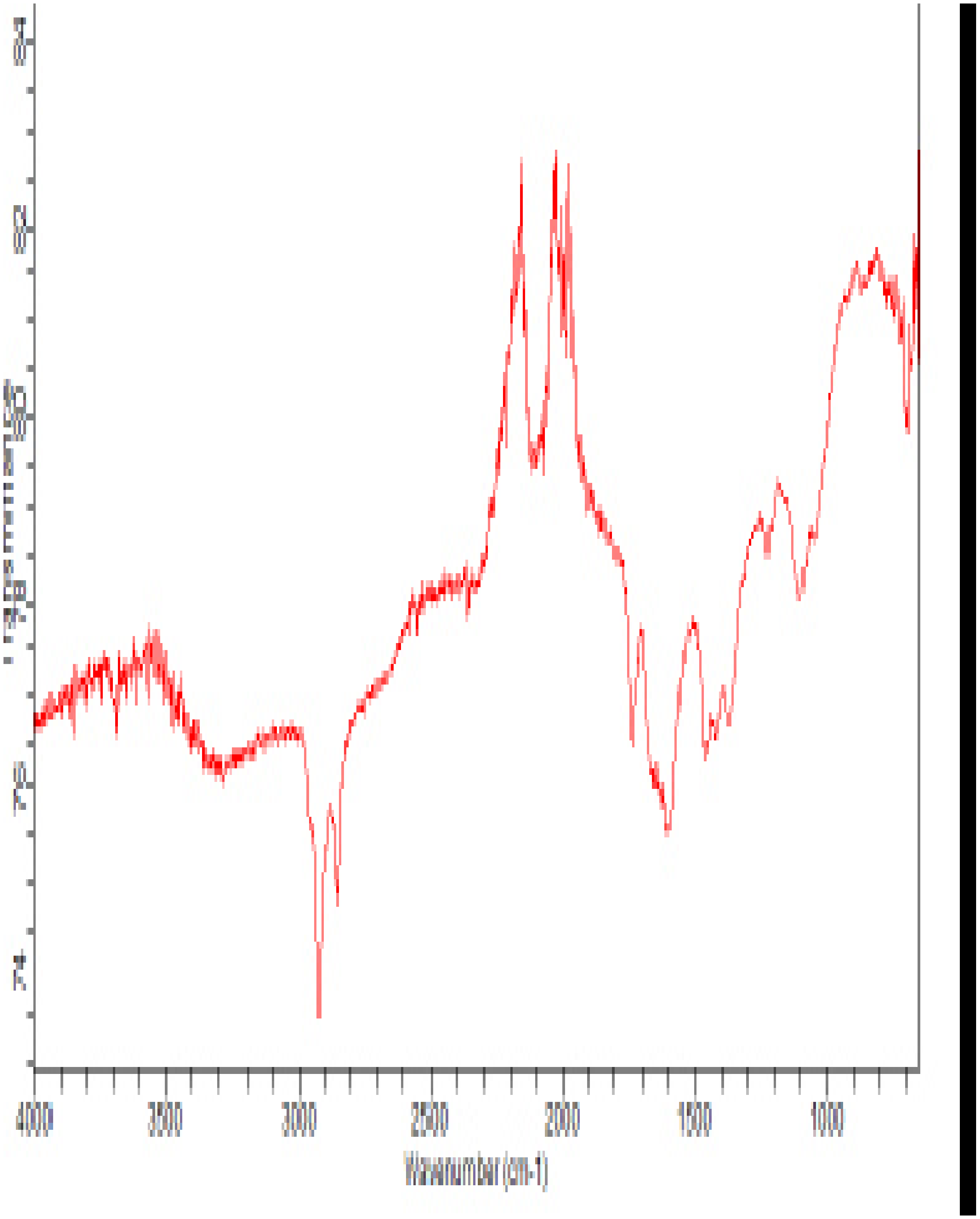


Figure 4.18: FTIR Absorbance Spectra of Tin Metal in 1.0M NaOH with *Lawsonia inermis*

4.2. DISCUSSION

4.2.1 Effect of Immersion Time

The result of weight loss variation with period of immersion for the corrosion of tin in 0.2 M solutions of HCl and NaOH without the inhibitor at 298 K temperature was presented in Fig. 4.1. The result obtained shows that, the weight loss of Tin metal in 0.2 M HCl and 0.2 M NaOH solutions increased with increased in time at 298K which indicated that the longer the time of the immersion tin coupon in the test solution the higher the weight loss due to corrosion resulting into higher corrosion rate. This is due to the interactions that occur between the acid or base and the metal surface contact in the solution, tend to destroyed tin surface gradually with time as a result of acid or base consumption by the metal there is progressive increased in the weight loss of the metal (Likhanova *et al., 2007).* In the early stage of the process it was observed that the weight loss differences from 1 to 6 hours are too small compared to longer time in which the tin metal was exposed to the corrosive environment as shown in the Fig. 4.1, meaning that there is a considerable weight loss differences from 6 to 12 hours and 12 hours to 24 hours respectively in the second stage. This shows that the more the metal is exposed to the test solutions, the more the contact between the interface, hence the greater the rate of dissolution resulting into a greater weight loss. Literature revealed similar trend of increase in weight loss with time (Ita *et al.*, 2013). This implies that corrosion is time dependent and can takes place even at lower concentration.

4.2.2 Effect of Corrodent Concentration

Tin corrodes in different concentrations of HCl and NaOH solutions at 298K, since there was a decrease in the original weight of tin as seen in Fig. 4.2. Weight loss was found to increase with increase in concentration of the acid and alkaline solutions but more in acid than in alkaline, which is the higher corrodent concentrations resulted into higher weight loss which in turn resulted into higher corrosion rate (Olivares-Xomelt *et al.,* 2006). The choice of immersion period (3hrs in acid and 4hrs in basic media) was based on the fact that the dissolution is faster in acidic medium than basic medium and that weight loss difference between the time interval from 4 to 6 hours is almost equal and was considered as the equilibrium time as seen in Fig. 4.1. The corrosion is attributed to the presence of water, air, and H^+, which accelerate the corrosion process (see the electrochemical reactions in chapter one). This observation is due to the fact that the rate of a chemical reaction increases as the concentration of active species (acid/ alkaline) increases and/or may be due to the increase in the rate of diffusion and ionization of active species in the corrosion reactions. This observation has been reported by several authors (James and Akaranta, 2009; Iloamaeke *et al.,* 2012). In their work on the inhibition of corrosion of zinc in 2.0 M hydrochloric acid solution with acetone extract of red onion skin, Corrosion inhibition of mild steel using *Pterocarpus soyauxi*.

4.2.3 Effect of Temperature on the Corrodent Concentration

The effect of the temperature on the corrosion rate (CR) of tin coupon immersed in 1 M HCl and 1 M NaOH solutions was evaluated by varying the temperature in the range 298 K - 323 K, without the inhibitor and at 303 K and 323 K in the presence of the inhibitor in both test solution for a period of 3 h and 4 h respectively. There is a slightly increase in weight loss as the temperature is increased from 298 – 323 K (Fig. 4.3). This observation implies that temperature favours the reactivity of the active constituents of the corrosion media. A rise in the temperature usually increases the rate of hydrogen evolution reaction on the cathode, which results in a higher metal dissolution rate. This shows that the dissolution of the metal coupons increased at higher temperatures. It is also evident that a combination of higher temperatures produced higher weight loss with time, thus higher rate of reaction. This observation is attributed to the general rule guiding the rate of chemical reaction, which says that chemical reaction increases with increasing temperatures. Also an increased temperature favours the formation of activated molecules, with 5°C rises in temperature, thereby increasing the reaction rate. This is because the reactant molecules gain more energy and are able to overcome the energy barrier more rapidly. An increase in temperature may also increase the solubility of the protective films on the metal, thus increasing the susceptibility of the metal to corrosion (James and Akaranta, 2009).

However, inhibition decreases with increase in temperature. From Table 4.2-4.5, it can be observed also that as temperature change from 323 K to 303 K in the presence of an inhibitor at optimum concentration, there is a corresponding decrease in the weight loss and decrease in the corrosion rate in the range 17520-110 mm/y resulted in the higher inhibition efficiency (93.1-95.45%; 77.1-85.19% and 44.8-54.55%; 71.4-77.78) for henna and caffeine in alkaline and acidic solution respectively. The maximum inhibition efficiency is lower at 323K than at 303K. This is in agreement with what is known about the dependence of adsorption on temperature, that as temperature rises, the quantity adsorbed decreases and as a result of this, the isotherm of higher temperatures are lower than that of lower temperatures. The higher corrosion rate observed at elevated temperature can be attributed to an appreciable increased in desorption of the inhibitor on the metal surface with increased in the higher temperature, therefore, the higher the temperature, the higher the rate of corrosion. The action of organic inhibitors depends on the type of interaction between the substance and the metallic surface. This could cause a change either in the electrochemical process mechanism or on the surface available to the process. The decrease in inhibition efficiency with increasing temperature, suggest weak adsorption interaction between tin surface and the inhibitor suggesting a physical adsorption mechanism due to the higher desorption of inhibitor molecules at higher temperature, the greater surface area of metal surface comes into contact with the media, resulting in increased corrosion rates with increasing temperature (Torchio, 1981).

The Arrhenius equation was adopted to study the effect of temperature on the rate of corrosion of tin metal containing various concentrations of the inhibitors and without inhibitor as expressed by equation (7). The calculated values are presented in Table 4.7 and 4.8. These values ranged from 19 to 29.5kJ mol^{-1} and are lowered than the threshold value of 80kJ mol^{-1} required for chemical adsorption, indicating that the adsorption of both compounds in Henna and Caffeine on tin metal surface confirms with the mechanism of physical adsorption (Nwabanne and Okafor, 2011).

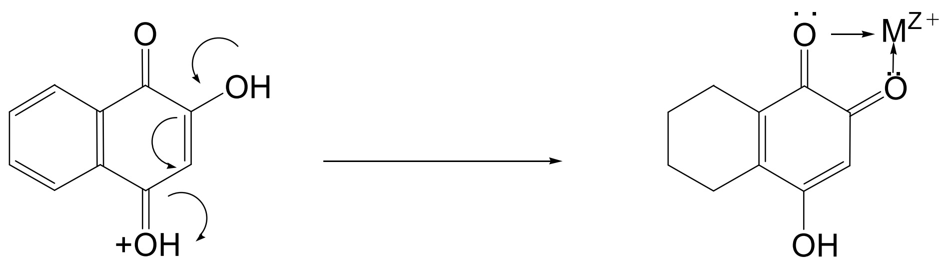
4.2.4 Effect of Inhibitor on the Corrosion Process

The effect of addition of Henna and Caffeine at different concentrations on the corrosion process of tin in 1.0 M HCl and 1.0 M NaOH solutions and to optimize the most suitable inhibitor concentration that leads to the lowest corrosion rate were studied at 3 h and 4 h respectively. There was a general reduction in the weight loss of tin sheet in the solutions containing *lawsonia inermis (Henna) and Caffeine (*Fig. 4.4) at 323 K compared to the uninhibited solutions. Percentage inhibition efficiency against inhibitor concentrations are presented in Fig. 4.5. It can be seen from the figure that the inhibition efficiency (%IE) of the inhibitors increased with increasing concentrations of inhibitors. The maximum inhibition efficiency (93.10%) was observed for *Lawsonia inermis (L)* at an inhibitor concentration of 0.5% in 1M NaOH solution for leaves extract whereas it was 46% in 1M NaOH solution with same concentration 0.5% for caffeine as presented at 323 K. Table 4.1 shows the variation of corrosion rate in the absence of the inhibitor at temperature range 298-323 K while the Tables' 4.2-4.5 in the presence of inhibitor with varying concentration of inhibitors, it also shows the values of inhibition efficiencies and degree of surface coverage obtained from weight loss measurement of different concentrations of Henna extract and Caffeine as compared to the weight loss and corrosion rates of tin in free acid and alkaline solutions at 303 and 323 K in a thermostatic water bath.. From the data it was observed that corrosion rate was significantly lowered down in presence of the inhibitors than in their absent and also it is clear that the surface coverage (θ) increases with increasing concentration of inhibitor but decreases with increase in temperature. This effect is hugely marked at optimum concentration (0.5%) of the inhibitors.

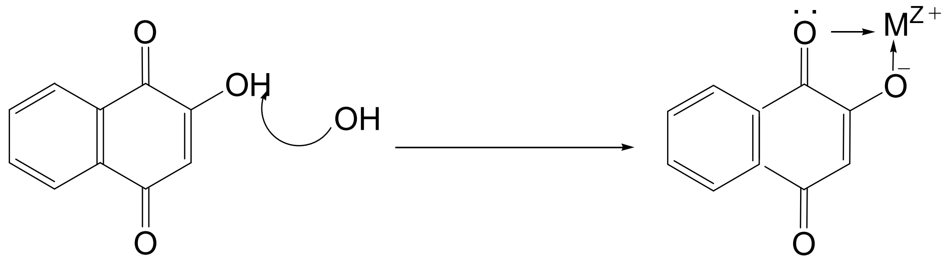
The corrosion rate was found dependent on the concentration of inhibitors and temperature, with the increased in concentration the corrosion rate decreased gradually. The decreasing corrosion rate and increasing inhibition efficiency was attributed to the fact that the adsorption of inhibitor on the metal surface blocked the corrosion sites of metal surface. This implies that the Henna extract and Caffeine bonded and adheres on the surface of corroding environment and produced a protective film on the metal. Analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies in the presence of inhibitor gives some insight into the possible mechanism of the inhibitor adsorption. A decrease in inhibition efficiency with rise in temperature, and there is analogous increase in corrosion activation energy in the presence of inhibitor compared to its absence, has been frequently interpreted as a suggestive of formation of an adsorption film of electrostatic physical nature, a trend similar to that reported by other authors (Ituen et al., 2013). The adsorbed films of the inhibitors act as physical barrier between metal surface and corrosion media (Hassan and Sisodia, 2011).

The lower weight loss of Henna in NaOH solution and higher weight loss of Caffeine in the same test solution marks a difference in the medium. This indicates that the tin sheet coupons corrode less with henna in the NaOH solution containing the inhibitor than in its absence due to the inhibitive action of *Lawsonia Inermis (L)*, but corrodes more with

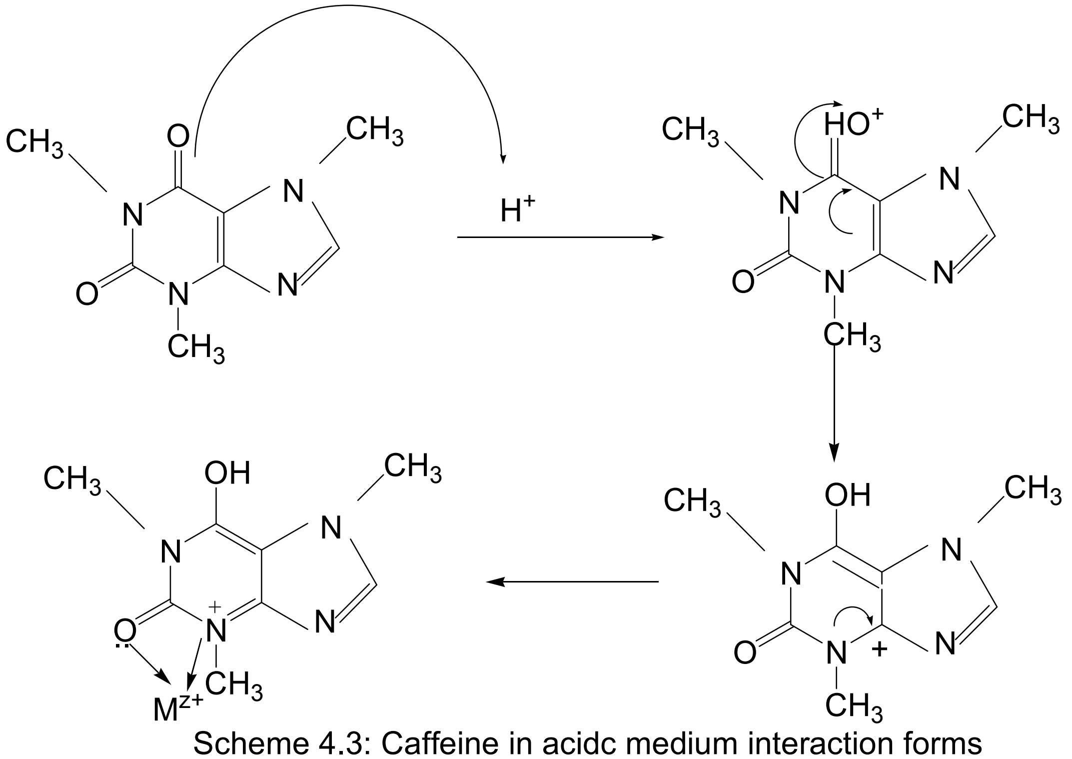
Caffeine (Cf) in NaOH solution. Likewise the henna performed better than caffeine in the acidic medium. Then Henna inhibitor studied inhibit the corrosion of tin in both media is found to exhibit the best inhibitory action. This observation implies that the presence of henna led to the formation of protective film and reduce the surface contact between the corrosive media and the metal, eventually retarded the dissolution of the metal in both acidic and alkaline media. The following mechanisms are proposed for the reactions of Henna and Caffeine in both acidic and basic media and the interaction with the metal (M).



scheme 4.1 : Henna in acidic medium forms of lawsone



Scheme 4.2 : Henna in basic medium forms of lawsone



Scheme 4.3: Caffeine in acidc medium interaction forms

In the acidic solution of Henna (Scheme 4.1), the oxygen atom of the lawsone of the inhibitor can be protonated easily, because there is high electron density on it s to positively charged inhibitor species while in the basic solution (Scheme 4.2), the hydrogen atom of the phenolic group in lawsone can be deprotonated by the high electron density of hydroxides ions from the base leading to negatively charged inhibitor species. The adsorption can occur via electrostatic interaction between the charged molecules and the charged on the metal surface leading to physisorption of the inhibitor molecules. Further co-ordinate bond may occur between unshared e^- pairs of unprotonated oxygen atom of the inhibitor and vacant d-orbital of metal surface atoms (Hamdy *et al.,* 2012). In the case of Caffeine, the oxygen atoms of C=O group in the inhibitor can also protonated easily due to high electron density on the inhibitor molecules with delocalization of electrons leading to negatively charged inhibitor specie as in the acidic solution (Scheme 4.3). The adsorption can be formed via electrostatic interaction between the charged inhibitor molecules and the charged on the metal surface leading to physisorption of the inhibitor molecules. Further co-ordinate bond may be linked the charged positive metal to the electron rich centre of $–OH^-$ group and the lone pair of nitrogen atom in the six member ring of the inhibitor.

The mechanism of the reaction study is not fessible at higher pH in the basic medium due to the lack of proton hydrogen in the caffeine ring structure in which the hydroxide ion,-OH^- from the base cannot be abstract from the ring in order to initiate the reaction. However the inhibitor was found from experimental results to attached its self to the tin metal through the C=O in the structure of caffeine, hence gives a low inhibition efficiency even at lower temperature in the basic solution contained caffeine.

From the result presented in Figs. 4.10 to 4.18 there is Tin interaction with Caffeine and Henna due to the differences in the spectral as indicated by peaks collections before and after immersion in 1.0M HCl and NaOH solution containing the inhibitors respectively. Literature shows that maximum inhibition efficiency for caffeine in mild steel is 92.4% and above 70% for Henna in acidic media and in good agreement with the present result. This observation is due to the presence of free oxygens located at position 2 and 6 as represented by the chemical structure of caffeine and likely the presence of π-electrons (Abiola and James, 2010). The result obtained is in good agreement with literature.

Metal surface contained traces of ethanol and acetone from bands around 3000 cm^{-1} and in the range 1800-650 cm^{-1}. The presence of ethanol and acetone continue to show in aqueous HCl solution; Bands around 3000 cm^{-1} and 1800-650 cm^{-1} due to solvents and around 3500 cm^{-1} is due to adsorbed water molecules. Figs. 4.13 and 4.14 are basically the same but more surface OH groups appear in Fig. 4.14. From Fig. 4.15 the surface groups, OH groups were displaced by Caffeine while solvent molecules still present in acid medium. Caffeine displaced most of solvent molecules in alkaline medium as observed in Fig. 4.16 presented.

The C=O bond ranges from 1630 to 1820 cm^{-1} (Francis, 2000). The FTIR spectrum of pure Caffeine is shown in Fig. 4.12. The C=O stretching frequency appears at 1648 cm^{-1}. The bands due to aromatic C-H stretch appear at 3112 and 2956 cm^{-1}. The band at 1480 cm^{-1} is due to C=N ring stretching. The CH_3 group absorptions $\delta_s CH_3$ in CH_3-N appears at1432 cm^{-1}.

The FTIR spectrum of the film formed on the metal surface after immersion in the solution containing 50 mg/L of Caffeine are shown in the Fig. 4.15 and 4.16. The C=O stretching frequency has shifted from 1648 cm^{-1} to 1742 cm^{-1} and 1743 cm^{-1} in HCl and NaOH solution respectively. This is due to the shift of the electron cloud of C=O bond toward Sn^{2+}/Sn^{4+} ion formed on the metal surface. This result in the formation of Caffeine-Sn^{2+} complex on the metal surface in the acidic medium while in basic medium, Caffeine-Sn^{4+} complex is formed on the metal surface. The C=N ring stretching has shifted from 1480 to 1451 cm^{-1} and 1438 cm^{-1} in the acidic and basic media respectively. This suggests that the electron cloud of C=N bond co-ordinates with Sn^{2+}/Sn^{4+} ions formed on the metal surface. Thus, FTIR spectral study imply that in the presence of Caffeine, the anodic reaction of tin metal dissolution is controlled by the formation of Caffeine- Sn^{x+} complexes on the anodic sites of the metal surface in the reactive media. Caffeine is coordinated to Sn^{x+} through the oxygen atom of the C=O group and the ring nitrogen, C=N in each of the media (Anthony et al, 2004).

The results were also confirmed by FTIR spectra of Plant extract and Sn-sheet surface immersed in 1 M HCl and 1 M NaOH with 50 mg/L of Henna extract (Fig. 4.11). The main constituent of Henna extract is lawsone (Scheme 1.1); it contains benzene unit, p-benzoquinone unit and phenolic group. The-OH bond ranges from 3200-3650 cm^{-1} (Robert and Francis, 1990). The phenolic –OH stretching appears at 3272 cm^{-1}. The peaks at 2920 and 2106 cm^{-1} can be assigned to aliphatic and aromatic C-H. The aromatic C=C stretching frequency appeared at 1441 cm^{-1}. The C=O stretching frequency appeared at 1728 cm^{-1}. The FTIR spectra of the protective film formed on the metal surface after immersion in HCl and NaOH solutions are shown in Figs. 4.17 and 4.18 respectively. It is found that almost all the peaks observed for Henna extract are also identified for Sn-sheet immersed in 1 M HCl and 1 M NaOH solution containing 50 mg/L of Henna extract. The phenolic –OH stretching has shifted from 3272 cm^{-1} to 3305 and 3650 cm^{-1} in the acidic medium and 3281 cm^{-1}, 3558 cm^{-1} in the basic medium. The aromatic C=C stretching shifted from 1441 cm^{-1} to 1460 $cm^{-1}$and 1458 cm^{-1} in the HCl and NaOH solution respectively. The C=O stretching frequency has been shifted from 1728 cm^{-1} to 1743 cm^{-1} in both HCl and NaOH solutions. This indicates formation of Tin-Plant extract complexes or salts. The phenol group of lawsone would donate electron to the metal in order to achieve its noble state of orbit, while the metal would receive the electron to become more stable. As a result of this phenomenon, the metal surface is protected from the corrosion attack by hindering the redox process (Hamdy *et al*, 2012).

4.2.5 Adsorption Isotherm

The interaction of Caffeine and Henna on the metal surface has been examined by the various adsorption isotherms. The degree of surface coverage values (ϴ) for various concentrations of the inhibitors in the solutions were estimated from the different adsorption isotherm model (equations 22-27). These equations were developed on the assumption that adsorption will only take place at specific homogeneous sites within the adsorbate surface with uniform distribution of energy level; this imply that adsorption process is monolayer in nature (Kaewprasit *et al*, 1998).The tests reveal that the adsorption of both Henna and Caffeine on tin surface is best described by Freundlich (0.997), Frumkin (0.990), Temkin (0.988), El-Awady (0.980), Langmuir (0.962) and Flory-huggins (0.886) adsorption isotherms in decreasing order based on plot correlation coefficient (R^2) values (Table 4.6). It indicates that the adsorbing species occupies typical adsorption site at the metal/solution interface as can be seen by the good fit inhibitors, which was found to obey freundlich adsorption isotherm model in acidic and alkaline media of both compound (Nnanna *et al.*, 2011a; Ituen *et al.*, 2013). The plots of the equations used are shown in Appendix 1.

Generally larger K values imply more efficient adsorption, hence a better inhibitive performance (Noor, 2009). The adsorption of both inhibitor used on to the surface of tin is retarded by increase in temperature supporting the mechanism of physical adsorption. Further elucidation of adsorption mechanism from the experimental data requires estimation of the adsorption modes of the inhibiting species (whether molecular or ionic). A negative surface charge will favour the adsorption of cations whereas anion adsorption is favoured by a positive surface charge (Popova *et al.*, 2007). The ability of Cl^- and OH^- ions in hydrochloric acid and sodium hydroxide to be strongly adsorbed on the metal surface and hence facilitate physical adsorption of inhibitor is an important consideration. The plot of logϴ against inhibitor concentration (mg/L) displays a straight line for the tested inhibitor in the acidic and alkaline media (Appendixes 1). The linear plots, with high correlation coefficient and slope of about unity in both media, clearly reveal that the surface adsorption process of the inhibitor molecules on the tin surface followed the Freundlich adsorption isotherm which gives relative higher values of K_{ads} = 0.06, 0.05; and 0.061,0.03 for both system in acidic and alkaline media respectively (Table 4.9). Therefore, one can conclude that adsorption occurred via physisorption mechanism.

4.2.6 Thermodynamic Study

The estimated values of Ea for the corrosion of tin in the absence and presence of the two inhibitors are listed in Table 4.7 and 4.8 respectively. From the result obtained the activation energy of basic medium was found to be higher than acidic medium which indicates reaction in basic solution require the higher energy as such take a longer time for corrosion of tin metal. The central idea here is that for the 1.0 M solution of the acid and base to attack the tin, its molecules must then be activated over an energy barrier equal to the Ea of the HCl and NaOH solutions and its temperature dependent. By the introduction of the inhibitor substances, the Ea values obtained in the presence of the inhibitors are greater than that of the HCl and NaOH solutions indicating deactivation of the acid or base molecules on collision with the metal surface thus reducing the rate of acid or base attack on the metal due to higher activation of the inhibited system. Cruz *et al,* (2004) reported that when the values of Ea >80 kJ/mol, it indicates chemical adsorption and when Ea <80 kJ/mol means physical adsorption. All the estimated values of the activated energy in this work were found to be less than 80 kJ/ mol which imply physical adsorption.

The standard free energy of adsorption, ΔG^0_{ads} was calculated by Equation (21) and presented in Table 4.9 which can characterize the interaction of adsorption molecules and metal surface. The negative values of ΔG^0_{ads} ensure the spontaneity of adsorption process as well as stability of the adsorbed layer on the tin surface. Generally, the value of ΔG^0_{ads} around -20kJ/mol or lower are consistent with physical adsorption (physicsorption), while those around -40kJ/mol or higher involve chemisorptions (Umoren *et al.,* 2006; Ebenso *et al*., 2009). The values of the free energy, ΔG^0_{ads} obtained are between -2 to -3.5 as presented in Table 4.9 for both inhibitors in the system which is consistent with literature and therefore confirms physical adsorption mechanism. Inhibitor raised the activation energy for the corrosion process making it difficult for the corrosion to take place. The increased in ΔG^0_{ads} as a result of the presence of the inhibitors in the system implied that corrosion less spontaneous or less likely to occur.

4.2.7 Kinetic Study

The plot of –log (weight loss) with time (Fig. 4.8) in the absence of the inhibitor is linear in the acidic medium (with almost a unity value for R^2) confirming that a first order kinetic is applicable to the corrosion of tin metal in the acid where as in basic medium it show a negligible value of R^2 non linear. Alternatively, a plot of 1/Wt.L versus time was linear with 0.873 values for R^2 in alkaline also indicated second order are more favourable in the base (Fig. 4.9). The calculated half-life and rate constant values are greater in base compared to acidic medium (Ituen *et al*., 2013). It has been reported by many researchers that most corrosion reactions obey the first order kinetic model (Liu *et al.,* 2009). The adsorption phenomenon can be explained using thermodynamic parameter which could be further supported with kinetic model to explain the mechanism of corrosion and inhibition process. The mechanism of inhibitor has been reported to be dependent on type, composition of metal and corrodent, structure, concentration and temperature of the inhibitor (Oguzie, 2007).

CHAPTER FIVE

5.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 SUMMARY

The corrosion properties, adsorptive and inhibitive properties of *Lawsonia inermis*, L (Henna) and caffeine were studied on tin metal surface corrosion in HCl and NaOH solutions using weight loss at lower and optimum temperatures. From the findings of this work, the study showed that tin metal has low corrosive effect both in acidic and basic media and more corroded in acid than in alkaline solution due to the longer period in basic medium. The reaction in acid followed first order kinetic while in alkaline it was found to obey second order with greater half-life. The inhibition efficiency and degree of surface coverage increased with increasing in inhibitor concentrations but decreased with increasing in temperature of the system for the both inhibitors but more efficient in Henna of alkaline solution up to 93.10% and that the inhibitor is efficient at temperature below 323K. The adsorption behaviour was approximated by Freundlich, Frumkin, Temkin, El-Awady, Langmuir and Flory-huggins isotherm which was found best fitted to obey Freundlich adsorption isotherm for both compounds in acidic and basic media respectively. The thermodynamics parameters; Activation energy (Ea) and free energy (ΔG) of uninhibited and the inhibited processes were also determined which indicated higher activation energy of inhibitors systems and lower values of free energy which shows the spontaneity and the physical adsorption mechanism of the process. The activation energy confirmed the adsorption mechanism. The study showed that both of the inhibitors are good corrosion inhibitors in both of the media.

5.2 CONCLUSION

In this research work, the corrosion behaviour of tin and the inhibition behaviour of *Lawsonia inermis* leaves extract and Caffeine on tin metal in 1M HCl and 1 M NaOH were investigated using weight loss method. The obtained results showed that, as the period of immersion increases, the weight loss due to corrosion also increasing over a longer period and the corrosion rate was found maximum comparatively in acidic medium than in basic medium with and without *Lawsonia inermis* leaves extract while Caffeine showed maximum corrosion rate in basic medium at a given time interval. Corrosion rate was also found to increase with increasing in corrodent concentration and temperature over time and the optimum temperature were determined at 50 ^{0}C in 1 M solutions. *Lawsonia inermis* leaves extract and Caffeine was found to inhibit the corrosion of tin by decreasing the corrosion rate comparatively in the acid and alkaline media. The inhibition was found to be maximum at an optimum concentration and low temperature due to the inhibitive action of *Lawsonia inermis* leaves extract and Caffeine. *Lawsonia inermis* leaves extract has proved to be an excellent inhibitor for tin in NaOH alkaline solution due to the presence of Lawsone. Inhibition efficiency of both inhibitors increases with increasing inhibitor concentration over the range 0.1% to 0.5%, the maximum inhibition efficiency was found up to 95.45% for tin in NaOH solution at a concentration of 0.5% for leaves extract whereas it was 77.78% for Caffeine with the same concentration in HCl acid at 303 K. Thus, it was concluded that *Lawsonia inermis* leaves extract is a better corrosion inhibitor than organic chemical like Caffeine. The adsorption takes place via physical adsorption mechanism and Freundlich adsorption model best described the inhibition process. The presence of the both compound adsorbed on the tin coupons was verified by spectroscopic measurements of the surface before and after corrosion tests. Thermodynamic parameters showed that the adsorption was spontaneous and the energy increase more than the activation energy of the uninhibited corrosion process leading to the formation of stable complex film on the metal surface. The kinetic parameters indicated the possible reaction mechanisms of the corrosion process to support those Equations (1-11) in Chapter 1.

5.3 RECOMMENDATIONS

Based on the present research studied, the following recommendations are suggested for consideration in order to ascertain and improve the experimental procedure and precision of the result.

1- Others methods like Polarization study, electrochemical impedance spectroscopy can be employ for monitoring corrosion rate.

2- Possibility of extending the immersion period up-till when the Coupon dissolves completely at a specified concentration.

3- Corrosion of tin below the room temperature should be investigate since tin is found to corrode less at lower temperature to find the temperature where there is no corrosion in an aqueous media.

4- Computational modelling can be employed to validate the quantum chemical theory of the results obtained experimentally and the use of density functional theory (DFT) to characterise molecular structures of the inhibitors.

5- Further investigation into the inhibition mechanisms is required to study the inhibitive action of Caffeine in the basic medium.

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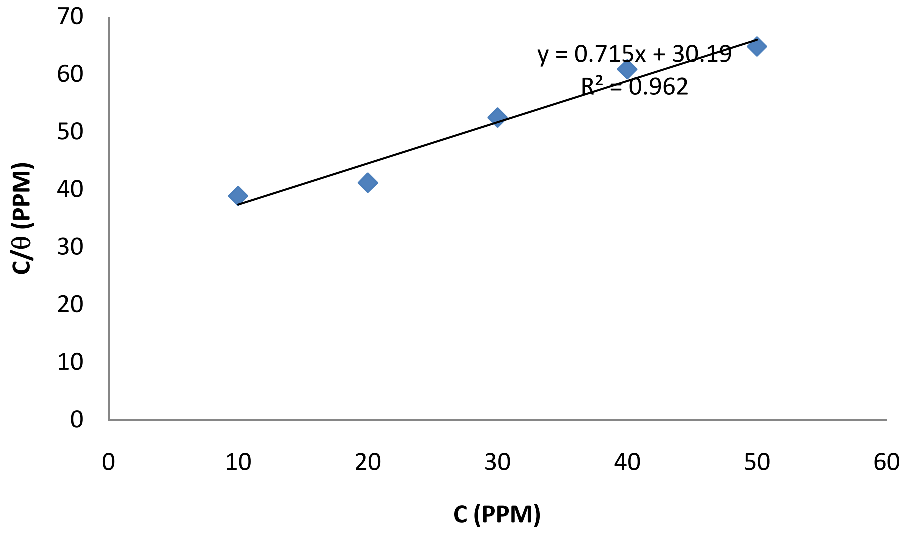
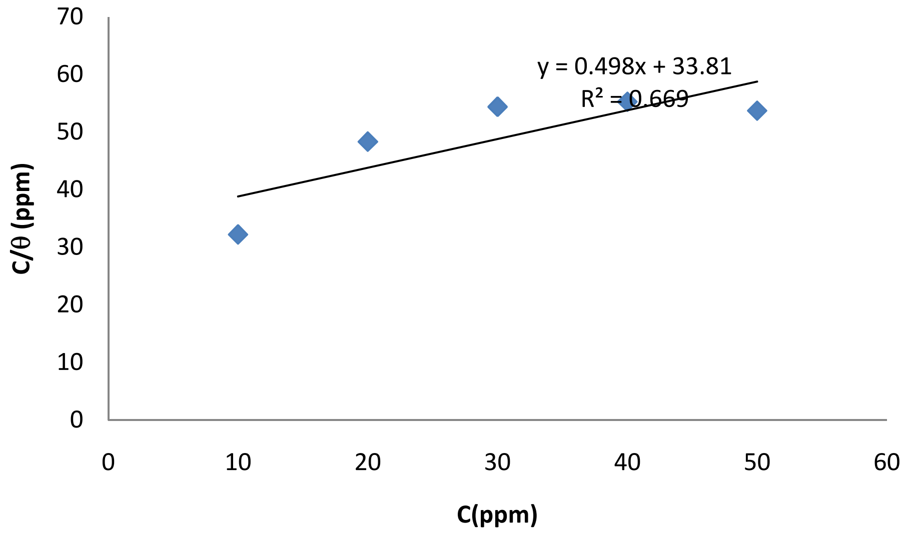
APPENDICES

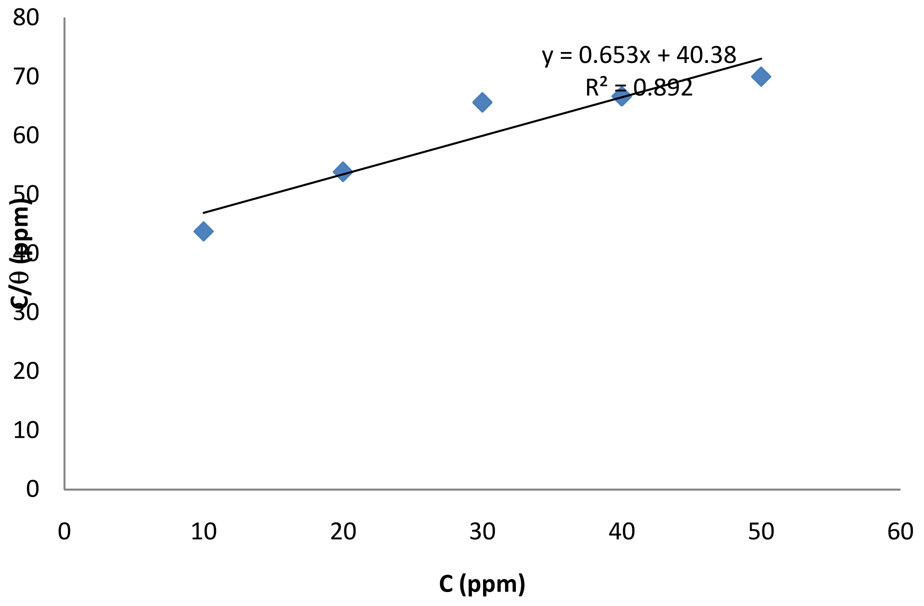
Appendix 1: Plots of Adsorption Isotherm Model



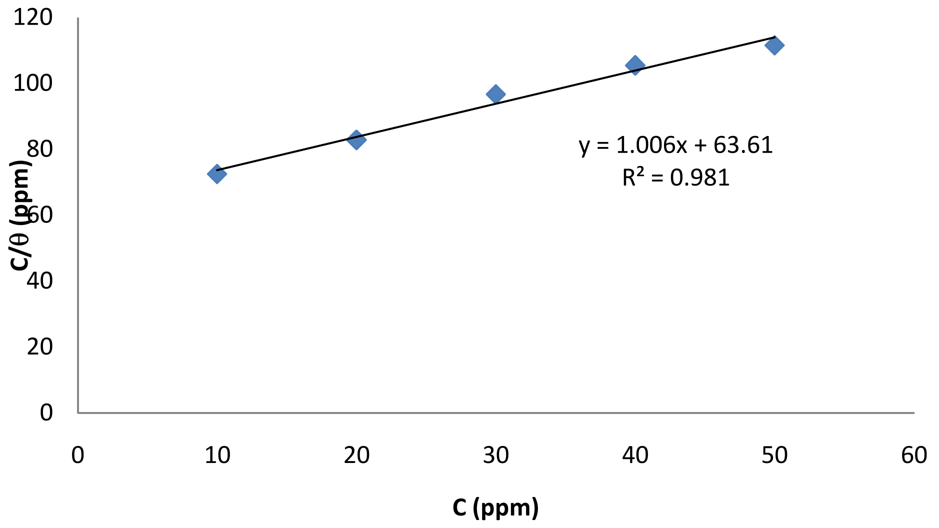
A: Langmuir Isotherm for Henna in the Acidic Medium



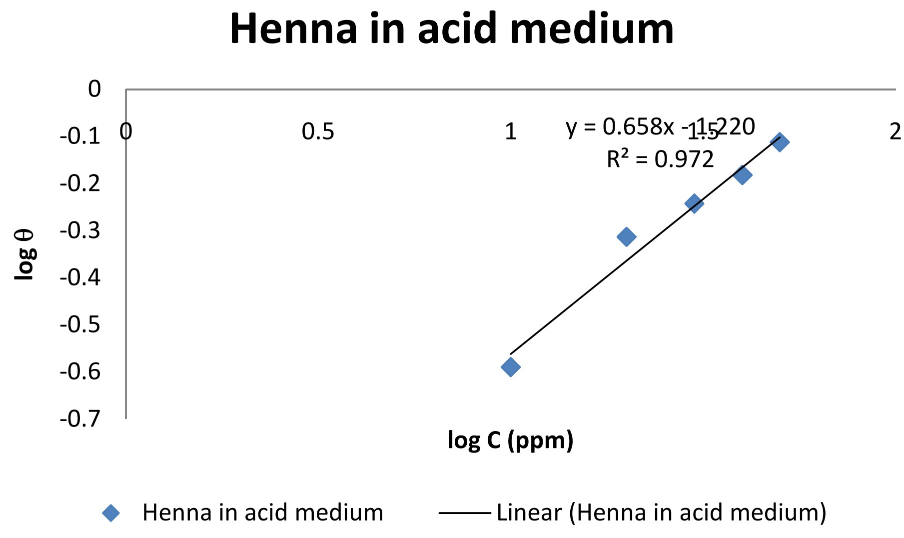
B: Langmuir Isotherm for Henna in the Basic Medium



C: Langmuir Isotherm for Caffeine in the Acidic Medium



D: Langmuir Isotherm for caffeine in the Basic Medium



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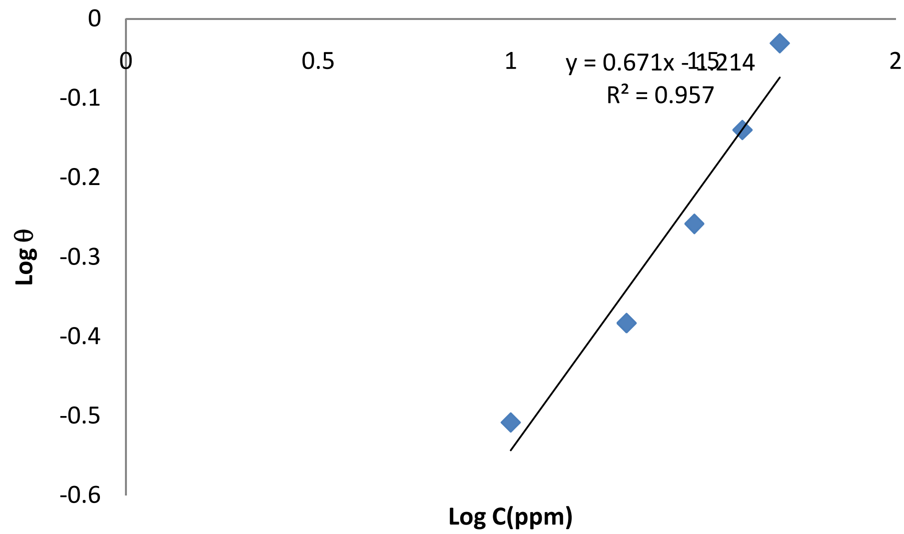
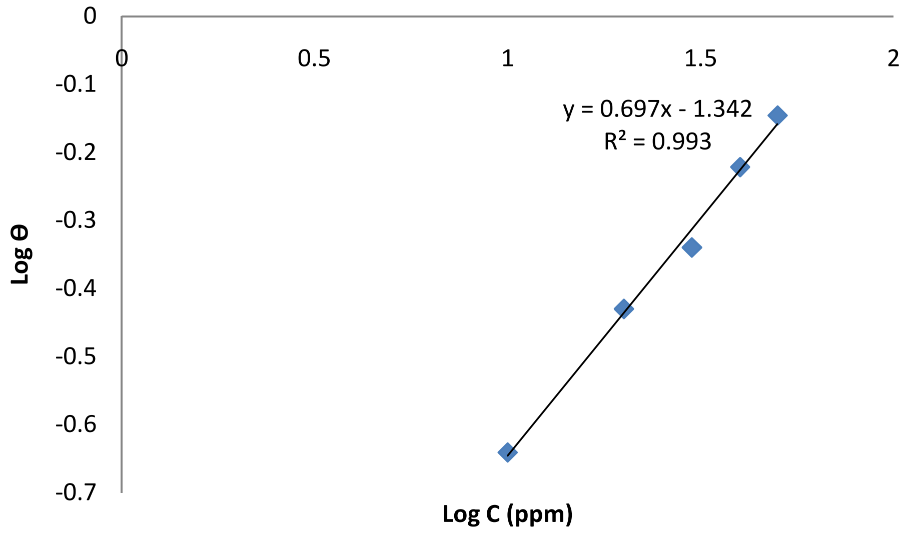
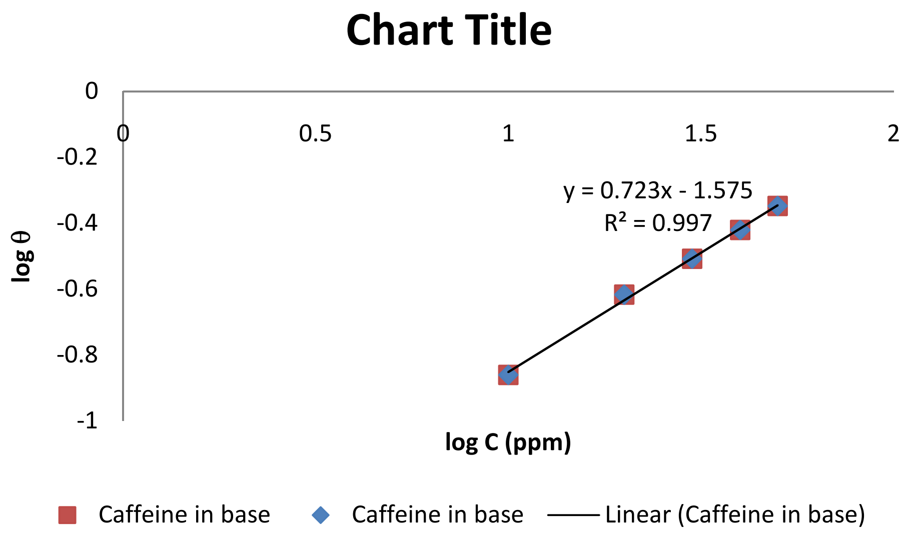


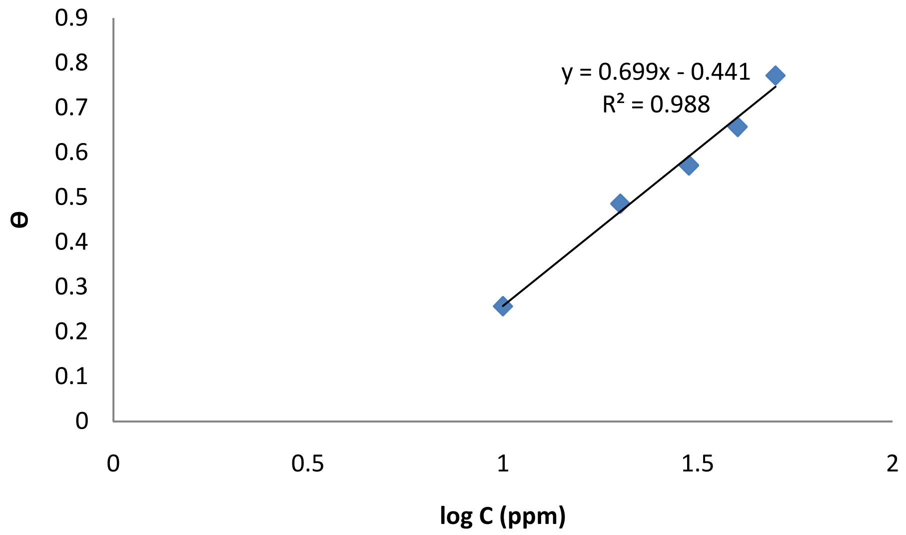
F: Freundlich Isotherm for Henna in the Basic Medium



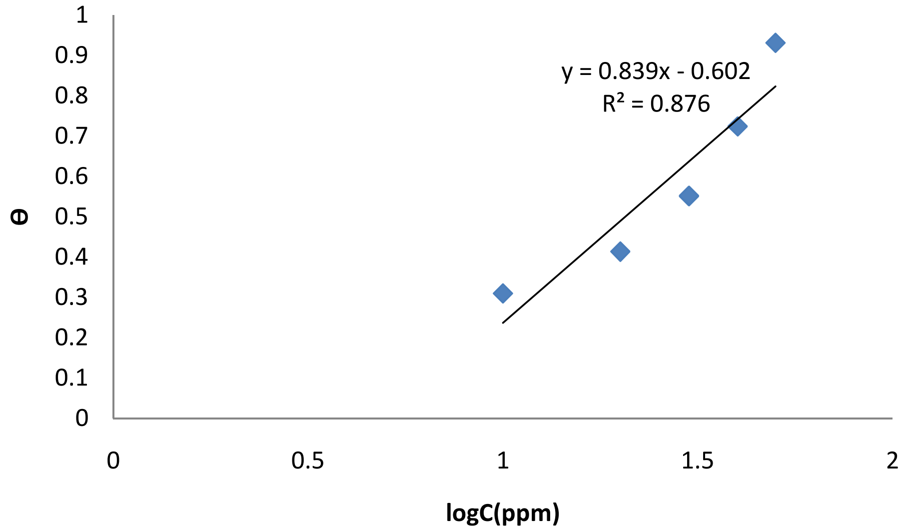
G: Freundlich Isotherm for Caffeine in the Acidic Medium



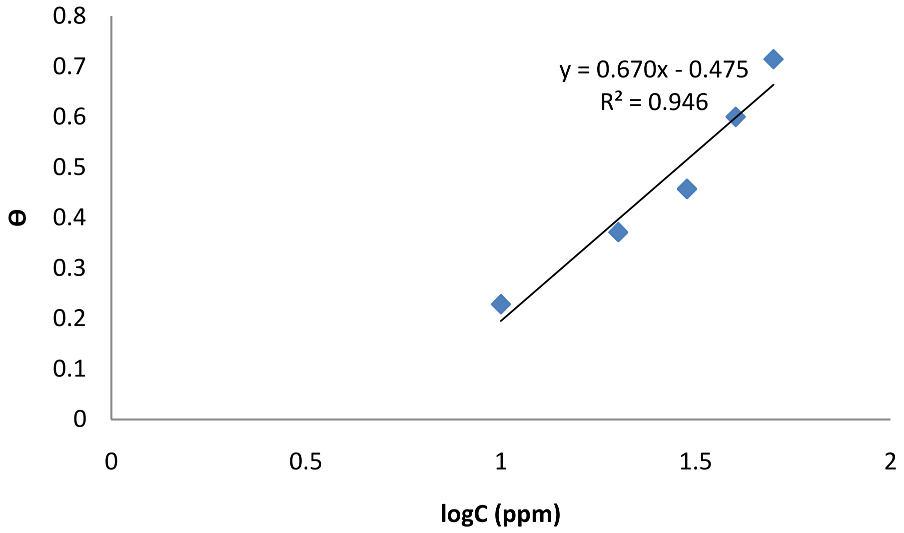
H: Freundlich Isotherm for Caffeine in the Basic Medium



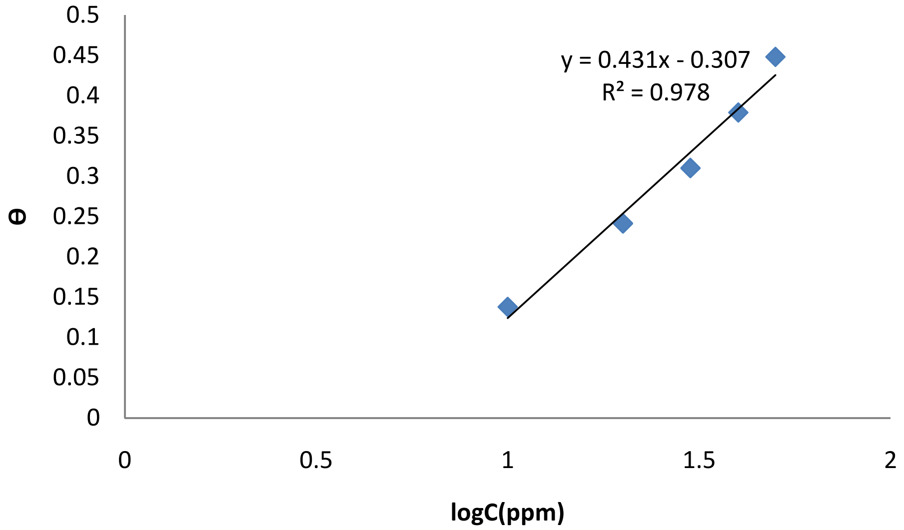
I: Temkin Isotherm for Henna in the Acidic Medium



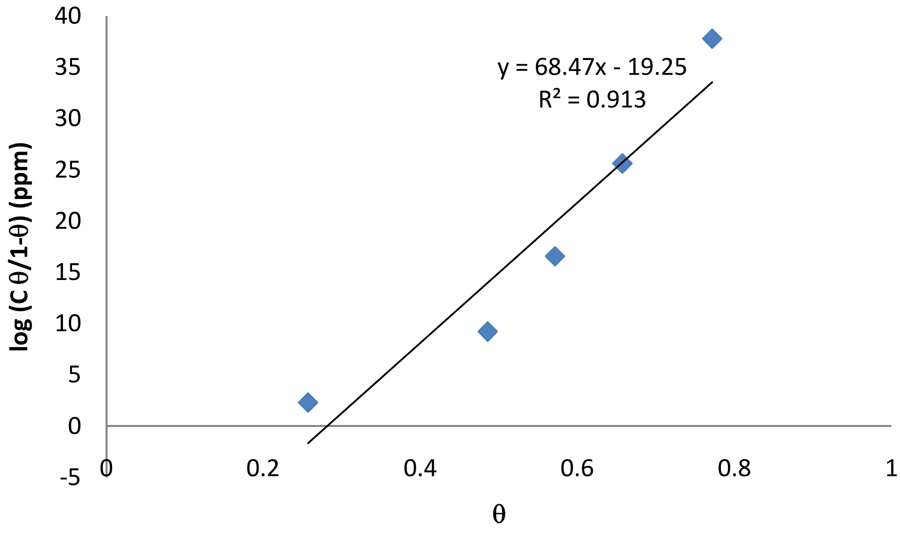
J: Temkin Isotherm for Henna in the Basic Medium



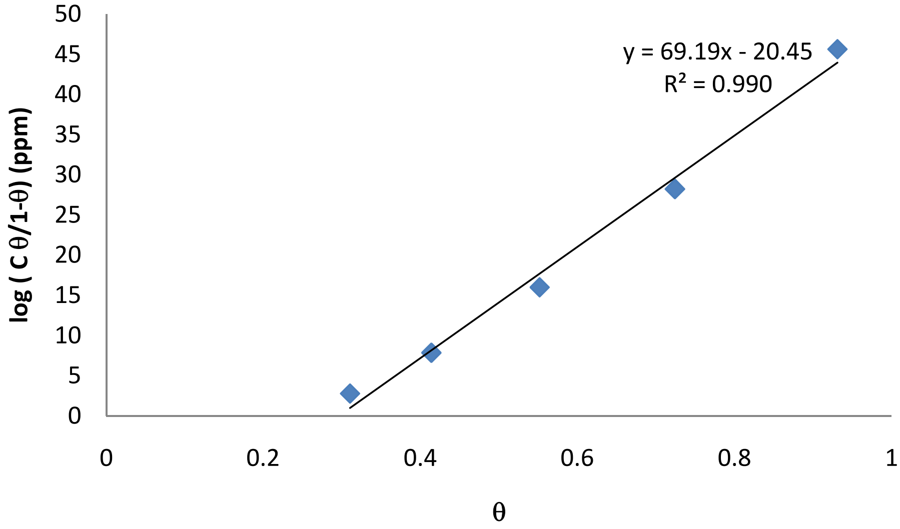
K: Temkin Isotherm for Caffeine in the Acidic Medium



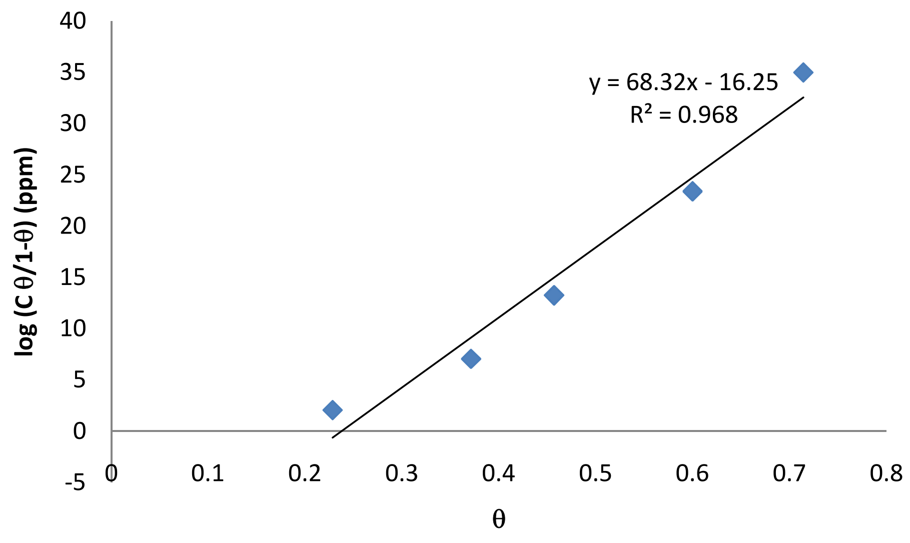
L: Temkin Isotherm for Caffeine in the Basic Medium



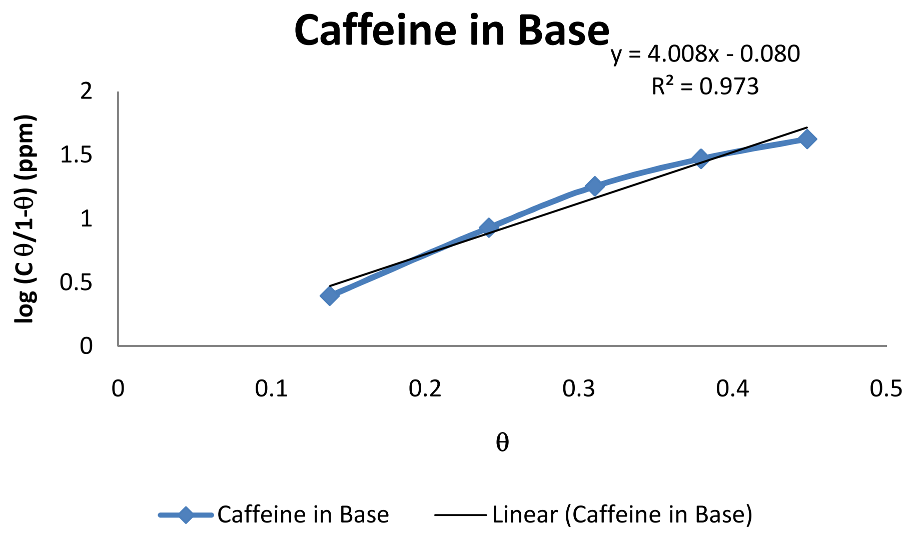
M: Frumkin Isotherm for Henna in the Acidic Medium



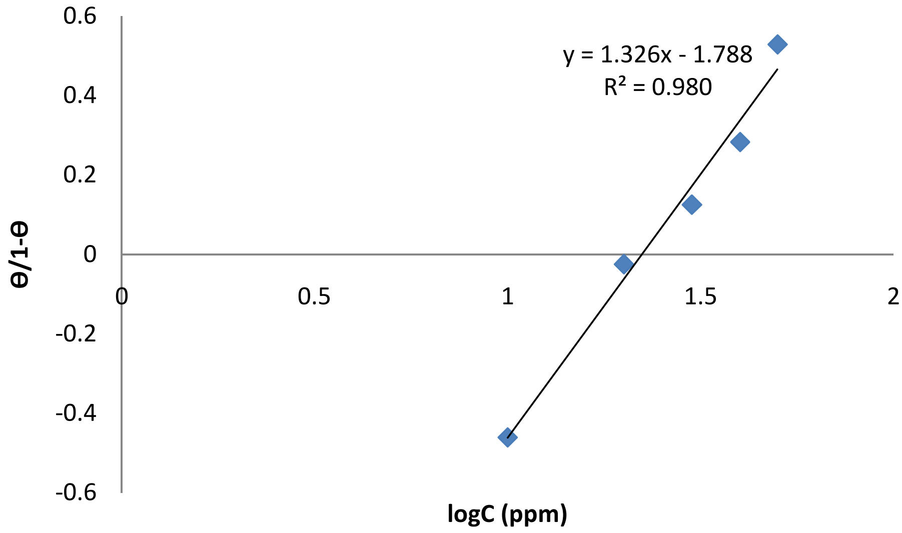
N: Frumkin Isotherm forHenna in the Basic Medium



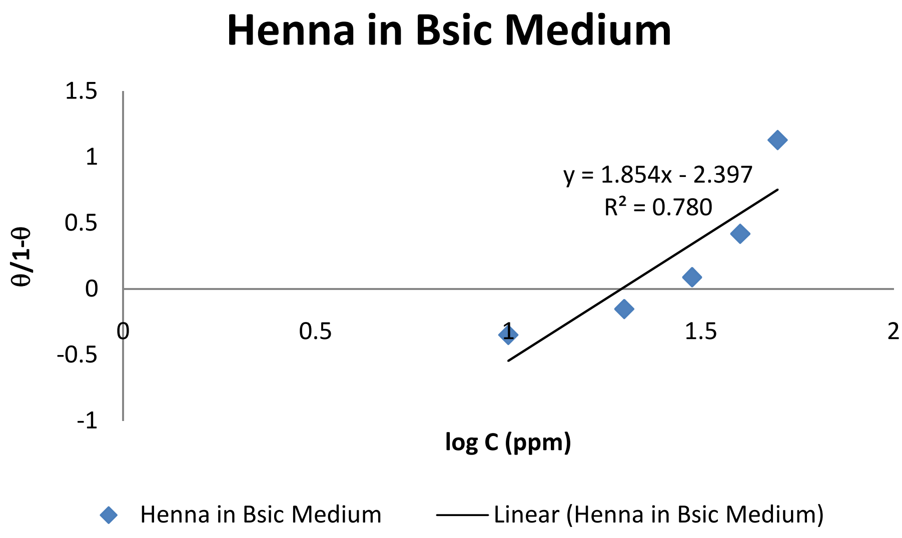
O: Frumkin Isotherm for Caffeine in the Acidic Medium



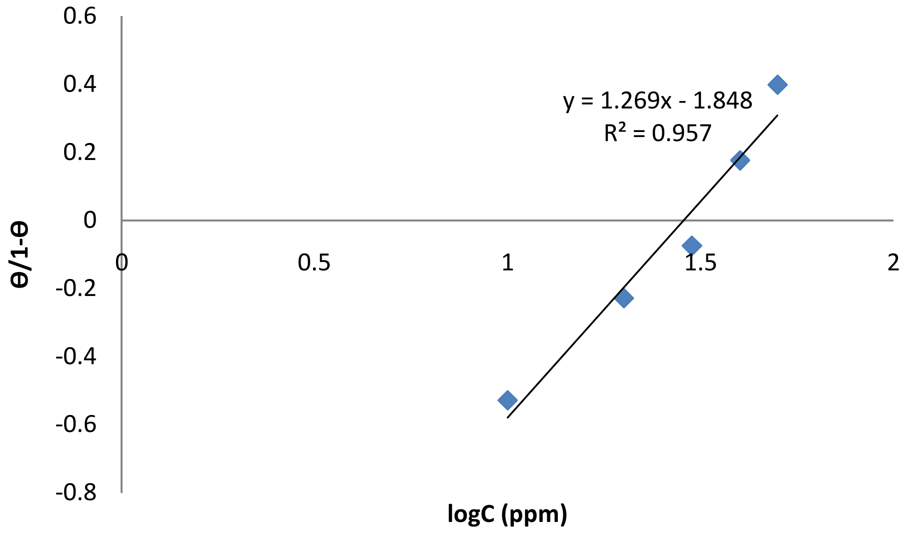
P: Frumkin Isotherm for Caffeine in the Basic Medium



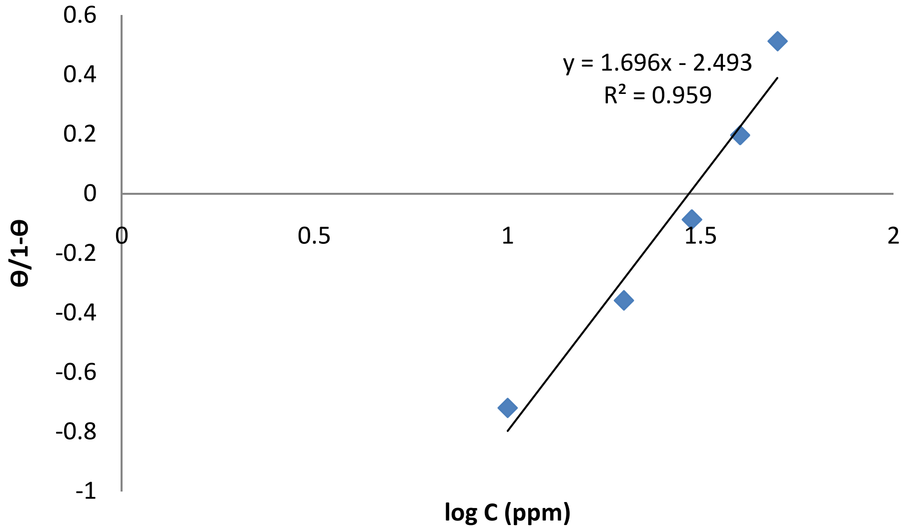
Q: El-Awady Isotherm for Henna in Acidic Medium



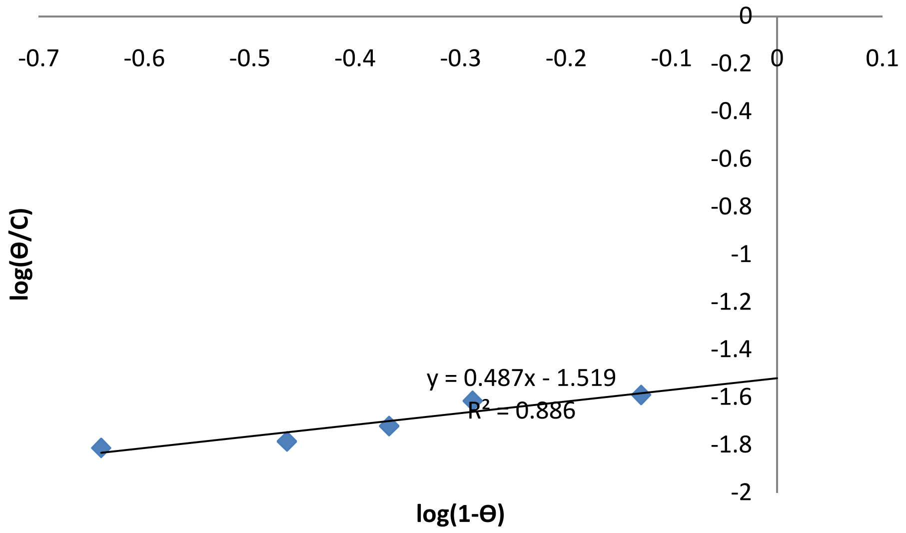
R: El-Awady Isotherm for Henna in Basic Medium



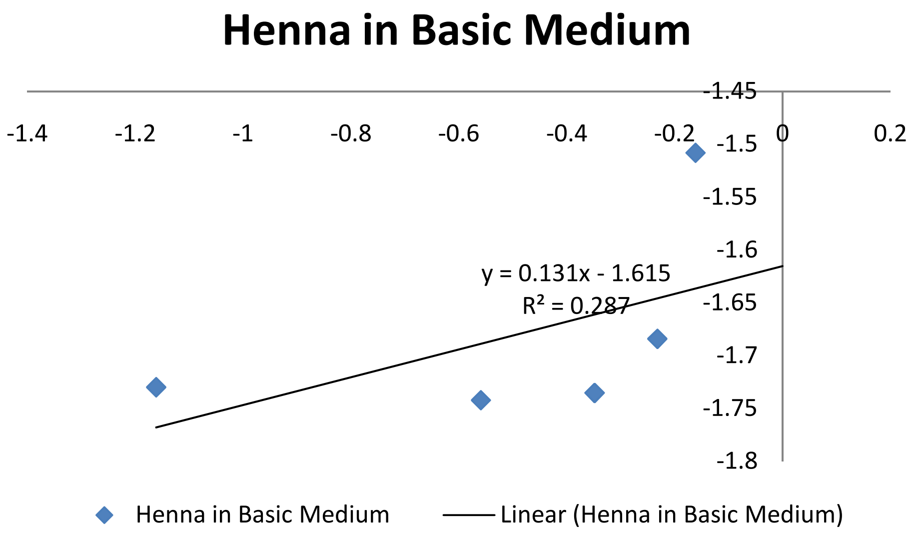
S: El-Awady Isotherm for Caffeine in the Acidic Medium



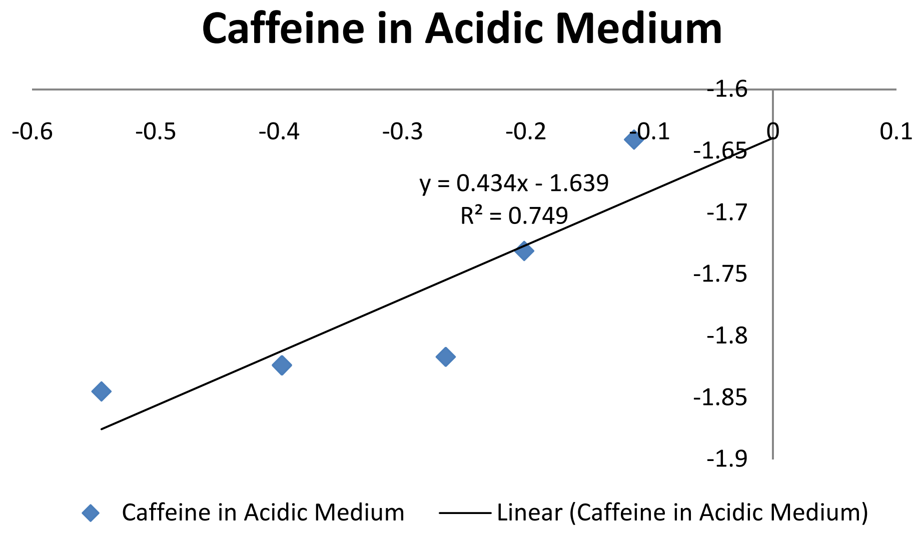
T: El-Awady Isotherm for Caffeine in the Basic Medium



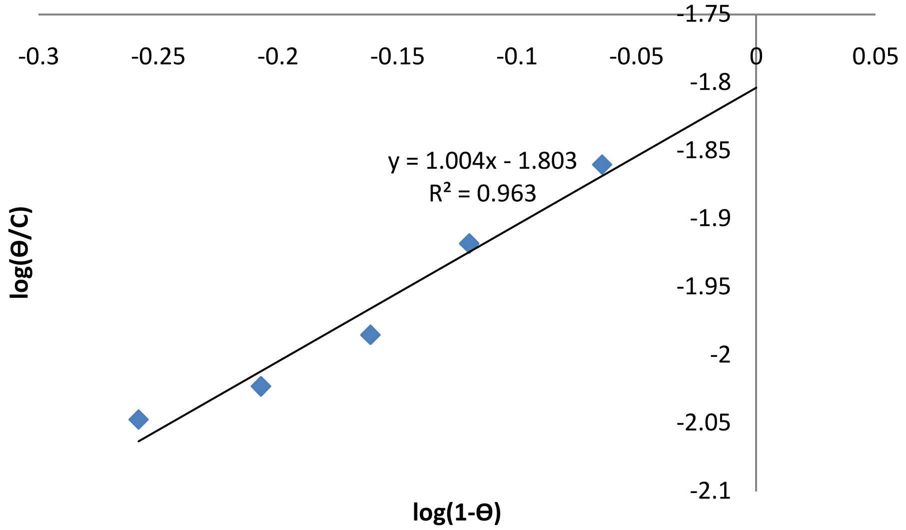
U: Flory-Huggins Isotherm for Henna in the Acidic Medium



V: Flory-Huggins Isotherm for Henna in the Basic Medium



W: Flory-Huggins Isotherm for Caffeine in the Acidic Medium



Flory-Huggins Isotherm for Caffeine in the Basic Medium

Appendix 2: Weight loss Data without the Inhibitor

Table 4.10: weight loss value in 0.2 M of Acid and Alkaline

S/N	Contact time(hr)	Average weight loss(Acid) (g)	Average weight loss(Base) (g)
1	1	0.0016	0.0007
2	2	0.0018	0.0010
3	3	0.0020	0.0011
4	4	0.0021	0.0015
5	5	0.0023	0.0017
6	6	0.0024	0.0019
7	12	0.0030	0.0023
8	24	0.0047	0.0034

Table 4.11: Weight loss value in varied Concentration of Acid and Alkaline

S/N	Concentration $(\frac{MOL}{dm^3})$	Average weight loss(Acid) (g)	Average weight loss(Base) (g)
1	0.20	0.0020	0.0015
2	0.40	0.0021	0.0016
3	0.60	0.0022	0.0017
4	0.80	0.0024	0.0018
5	1.00	0.0026	0.0021

Table 4.12: Weight loss value for varied Temperature in 1.0M Acid and Alkaline

S/N	Temperature (K)	Average weight loss(Acid) (g)	Average weight loss(Base) (g)
1	298	0.0026	0.0021
2	303	0.0027	0.0022
3	308	0.0028	0.0024
4	313	0.0030	0.0026
5	318	0.0032	0.0027
6	323	0.0035	0.0029