CORROSION INHIBITION OF MILD STEEL IN 1 M HYDROCHLORIC ACID SOLUTION BY *CYMBOPOGON CITRATUS* LEAVES EXTRACT

by

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LIST OF SYMBOLS

Symbol	Description	Unit
a	Interaction parameter	Dimensionless
A_s	Area of metal surface	cm^2
A	Pre-exponential factor	Dimensionless
C_{inh}	Concentration of inhibitor	g/L
CR	Corrosion rate	mm/yr
E_a	Activation energy	kJ/mol
$\Delta G°_{Ads}$	Gibbs free energy of adsorption	kJ/mol
$\Delta H°_{Ads}$	Enthalpy of adsorption	kJ/mol
K	Equilibrium constant	L/g
η_w	Inhibition efficiency	%
ρ	Metal density	g/cm^3
R	Molar gas constant	J/mol.K
R^2	Correlation coefficient	Dimensionless
$\Delta S°_{Ads}$	standard adsorption entropy	kJ/mol
t	Time of exposure	hour
T	Absolute temperature	K
W	Weight of mild steel	mg
ΔW	Weight loss of mild steel at specified time	mg
θ	Surface coverage	Dimensionless

LIST OF ABBREVIATIONS

FT-IR	Fourier Transform Infrared Spectroscopy
EIS	Electrochemical Impedance Spectroscopy

PERENCATAN KAKISAN TERHADAP KELULI LEMBUT DI DALAM 1 M LARUTAN ASID HIDROKLORIK DENGAN MENGGUNAKAN EKSTRAK DAUN *CYMBOPOGON CITRATUS*

ABSTRAK

Kesan perencatan bagi ekstrak *Cymbopogon Citratus* terhadap kakisan keluli lembut di dalam larutan 1M asid hidroklorik telah dikaji melalui ukuran penurunan berat logam. Kadar kakisan keluli lembut telah menurun dengan kehadiran ekstrak *C. citratus*. Kecekapan perencatan menaik apabila kepekatan ekstrak *C. citratus* menaik sehingga 2 g/L untuk mendapat kecekapan sebanyak 92% pada suhu 30 °C. Kesan terhadap suhu, kepekatan acid dan masa rendaman terhadap kadar kakisan keluli lembut juga telah dikaji. Analisis spektroskopi *Fourier Transform Infrared (FT-IR)* juga dijalankan bagi mengenalpasti ciri-ciri perencatan kakisan yang wujud di dalam ekstrak tumbuhan ini. Hasil kajian menunjukkan bahawa penjerapan ekstrak terhadap permukaan keluli lembut mengikut isoterma penjerapan *Langmuir* dan mekanisme penjerapan fizikal.

CORROSION INHIBITION OF MILD STEEL IN 1 M HYDROCHLORIC ACID SOLUTION BY CYMBOPOGON CITRATUS LEAVES EXTRACT

ABSTRACT

The inhibitive effect of naturally available *Cymbopogon citratus* leaves extract toward the corrosion of mild steel in 1M hydrochloric acid (HCl) solution has been investigated by weight loss measurement. The corrosion rate of mild steel was decreased in the presence of *C. citratus* extract. The corrosion inhibition efficiency increases on the increasing *C. citratus* extract concentration until 2 g/L to attain about 92% at 30°C. The effects of temperature, acid concentration and immersion time on the corrosion rate of mild steel in HCl solution either in the absence or presence of *C. citratus* extract were also studied. Fourier Transform Infrared (FT-IR) spectroscopy analysis was also carried out to establish the corrosion inhibitive properties of this plant extract in HCl solution. The results showed that the adsorption of the extract on the mild steel surface obeys Langmuir isotherm and physical adsorption mechanism.

CHAPTER ONE

INTRODUCTION

1.1   Research Background

Mild steel, also known as plain carbon steel is a major material of construction and broadly used in various industries especially in the oil and gas industry due to its strength, tensile, good physical property and relatively inexpensive cost. Besides, it is also widely used in chemical and allied industries for handling alkalis, acids, and salt solutions. For example, inorganic acids like hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) are used for drilling operations in oil exploration, descaling operations and in many industrial applications. However, one of the most challenging and difficult tasks for industries is the protection of metals from corrosion which makes it a critical problem that need to be solved.

Corrosion control of metals and alloys is an expensive process and industries spend massive amounts to control this problem. It is estimated that the cost of corrosion in the developed countries such as the U.S. and European Union is about 3 –5 % of their gross national product (Otaibi et al., 2014). Besides economic implications, corrosion also affects the safety and health of people who are working in industries or living in nearby towns. To prevent this issue, numerous methods such as upgrading materials, blending of production fluids, process control and chemical inhibition can be used. Among these methods, the use of corrosion inhibitors is the most economical and practical method in reducing corrosive attack on metals.

The inhibitors act by adsorbing onto the metal surface, thus providing a barrier to the corrosive environment. The inhibitors that previously used is inorganic inhibitors. However, those inhibitors containing phosphate, chromate and other heavy

metals are now being gradually banned by various environmental regulations because of toxicity and the environmental hazards they create (Roy et al., 2014). Similarly, synthetic organic inhibitors also being marred by their toxicity and high cost of manufacturing (Chigondo and Chigondo, 2016). In fact, the use of toxic material as corrosion inhibitors has been limited by agencies such as the U.S. Environmental Protection Agency (EPA), U.S. Department of Transportation (DOT) and Occupational Safety and Health Administration (OSHA). Hence, there is a strive to make use of environmental friendly, non-toxic and extracts of naturally occurring plant materials as corrosion inhibitors (Khan et al., 2015).

Extracts of plant materials contain a wide variety of organic compounds. Most of them contain heteroatoms such as phosphorus, nitrogen, sulphur, and oxygen. These atoms coordinate with the corroding metal atom (their ions), through their electrons (Orie et al., 2015). Hence, the corrosion is prevented when protective films are formed on the metal surface. In facts, natural inhibitors pose much lower risks in terms of handling and impact on humans and the environment. Furthermore, due to their natural availability, they are easier to produce and cheaper to buy. However, several conditions must be fulfilled for the selection of a suitable inhibitor such as the cost and amount of the inhibitors, long term toxicological effects, and the inhibitor's availability and stability in the environment (Khan et al., 2015).

1.2   Advantages and Limitations

In recent years, many alternative eco-friendly corrosion inhibitors have been developed due to the growing interest and attention of the world towards the environment and the hazardous concern. Thus, the extract of natural plants have been investigated. These extracts can be obtained in a simple way and purification methods are not required. The advantages of extract of natural plant as the alternative for the corrosion inhibitors are environmentally friendly, low toxicity, relatively less expensive, and readily available in plenty. It also has an ability to protect the metal surface efficiently in small quantities concentration and easily biodegradable. However, this biodegradability limits the storage and long-term usage of plant extracts. Thus, addition of biocides such as sodium dodecyl sulphate and N-cetyl–N,N,N-trimethyl ammonium bromide has been proposed to minimize this disadvantage (Sangeetha et al., 2011).

1.3   Problem Statement

Malaysia has been one of the most extensive natural gas pipeline networks in Asia since the Peninsular Gas Utilization (PGU) project had been completed in 1984. Currently, more than 2,500 km of main and lateral pipelines to transmit gas to the customers. The PGU pipeline is linked to the Trans Thailand-Malaysia (TTM) Gas Pipeline system in the north. The condition of the pipeline and its railways must always be inspected to ensure the pipeline does not have any leaking and damages due to corrosion. In fact, mild steel that is used in piping system has low carbon content which prone to corrode easily.

The high risk of corrosion attacks on pipeline become more serious as the pipelines were used for decade to transporting the chemical, liquid or gas. Pipelines that were buried underground transport whether crude oil, gas or water will across

various corrosive environment such seawater (offshore) and soil (onshore) that may lead into the corrosion attack and finally leaking the pipelines. However, corrosion control of metals and alloys is an expensive process and industries spend huge amounts to control this problem (Otaibi et al., 2014). Thus, various methods have been used to control the rate of corrosion of metals and alloys in industrial equipment. One of these methods is using corrosion inhibitors (Fattah and Noori, 2016).

Though many synthetic compounds have shown good anticorrosive activity, most of them are highly toxic to both human beings and environment. The safety and environmental issues of corrosion inhibitors arisen in industries has always been a global concern. These toxic effects have led to the use of natural products as anticorrosion agents which are eco-friendly and harmless. In recent days, many alternative eco-friendly corrosion inhibitors have been studied and developed, they range from rare earth elements to organic compounds (Patel, 2013). Most of the natural products are non-toxic, biodegradable and readily available in plenty. In addition, the cost of using green inhibitors is very less when compared to that of organic inhibitors which takes lot of chemicals and also time for its preparation (Sharmila et al., 2010). Hence, in an attempt to find corrosion inhibitors which are environmentally safe and readily available, extract of *C. citratus* leaves were collected and evaluated for its corrosion inhibition performance. The inhibition of *C. citratus* plant extracts also known as lemongrass were studied and investigated thoroughly on a mild steel specimen sheet in aqueous 1 M HCl solution. The investigation was conducted at room temperature as well at elevated temperatures such as 30°C, 40°C, 50°C and 60°C. Corrosion weight loss technique was applied to evaluate inhibition efficiency in the presence of this plant extracts as corrosion inhibitors.

1.4   Objectives

The main research objectives are:

I.   To characterize the functional group of *C. citratus* extract using Fourier transform infrared (FTIR) spectroscopy

II.   To determine the optimum condition for inhibition process of *C. citratus* extract on mild steel in 1 M hydrochloric acid solution in the range of operating parameters studied.

III. To study the adsorption mechanisms and kinetics of *C. citratus* extract on mild steel surface.

IV.   To determine the thermodynamics parameters and activation energy of acid corrosion on mild steel using Arrhenius equation.

CHAPTER TWO

LITERATURE REVIEW

2.1   Mild Steel

Mild steel is a type of carbon steel with a low amount of carbon, also known as "low carbon steel." It is not an alloy steel and therefore does not contain large amounts of other elements besides iron. The lack of alloying elements such as those found in stainless steels means that the iron in mild steel is subject to oxidation (rust) if not properly coated. However, the affordability, weldability, and machinability of mild steel make it such a popular choice of steel for consumers.

Mild steel is a major material of construction and broadly used in chemical and allied industries for handling alkalis, acids, and salt solutions due to its strength, tensile and good physical property. However, one of the most challenging and difficult tasks for industries are the protection of mild steel from corrosion. Mild steel reacts chemically/electrochemically with corrosive medium to form a stable compound, in which the loss of metal occurs. The compound formed is called corrosion product and metal surface becomes corroded. The current corrosion control of metals is an expensive process and industries spend huge amounts to control this problem.

2.2 Corrosion

The word corrosion is derived from the Latin 'corrosus' which means eaten away or consumed by degrees is an unpleasant word for an unpleasant process (Tringham, 1958). Corrosion is a natural occurring process where it can be defined as the interaction (electrochemical reaction) of a metal with the surrounding environment, causing a slow, steady, and irreversible deterioration in the metal, in both physical and chemical properties (Palou et al., 2014). It is a constant and continuous issue, often difficult to avoid completely. Thus, extreme care is required to minimize the corrosion rate. Based on Palou et al. (2014) also, the factors that can cause corrosion can be identified as physical, chemical, electrochemical and microbiological.

In general, physical corrosion is caused by impact, stress or exhaustion of the material while chemical corrosion is caused by oxygen, sulfur, fluorine, chlorine or other gases, which act directly on the metal under environmental conditions that facilitate this phenomenon. Electrochemical corrosion is defined as a spontaneous process that denotes the existence of anodic and cathodic zones, and an electrolyte while microbiological corrosion is the deterioration of a metal that occurs directly or indirectly as a result of the activity of microorganisms such as bacteria and algae. The rate of corrosion depends upon the environment and the type of material used. It can be very rapid in a highly corrosive environment or take years in a slightly corrosive environment (Palou et al., 2014). In chemical industries, many acidic solutions such as sulphuric acid, hydrochloric acid and phosphoric acid are extensively used during the acid pickling, acidic cleaning and petrochemical process. These industrial process lead to serious impairment of the metals and their alloys (Obot et al., 2013).

2.2.1 Types of Corrosion

The corrosion behavior of engineering materials is influenced by many factors such as material (chemical composition of metal), chemical environment (chemical composition of environment), physical parameter (temperature) and mechanical force (tensile stress). According to the environment to which materials are exposed, corrosion damage can be grouped into eight types. These types of corrosion are briefly described in Table 2.1.

Table 2. 1   Types of corrosion (Landolt, 2007).

Types of corrosion	Description
Uniform corrosion	Loss of material distributed uniformly over the entire surface exposed to the corrosive environment.
Galvanic corrosion	Results from the formation of an electrochemical cell between two metals. The corrosion of the less noble metal is thus accelerated.
Crevice corrosion	Caused by a difference of oxygen availability between two sites on a passive metal that leads to the formation of an electrochemical cell.
Pitting corrosion	Observed on passive metals in presence of certain anions (in particular chloride) when the potential exceeds a critical value.
Intergranular corrosion	Selective attack of grain boundaries.
Selective corrosion	Called selective leaching or dealloying, implies the selective dissolution of one of the components of an alloy that forms a solid solution. It leads to the formation of a porous layer made of the more noble metal.
Erosion corrosion	Result of an electrochemical reaction combined with a material loss by mechanical wear due to impingement of solids or a fluid.
Stress corrosion cracking	Results from the combined action of corrosion and of mechanical stress.

2.2.2 Corrosion Mechanism

The corrosion of metals is due to an irreversible oxidation-reduction (redox) reaction between the metal and an oxidizing agent present in the environment. Pure metals and alloys react chemically/electrochemically with corrosive medium to form a stable compound, in which the loss of metal occurs (Raja and Sethuraman, 2008). The effect of this process is that the metal surface becomes corroded. Anode is the area where iron atoms are oxidized while cathode is the area where reducing species such as non-metallic element or another metallic ion are reduced.

The following reaction equation is the example of corrosion of iron in the presence of hydrochloric acid.

$$Fe(s) + 2\ HCl(aq) \rightarrow FeCI_2(aq) +\ H_2(g) \qquad (2.1)$$
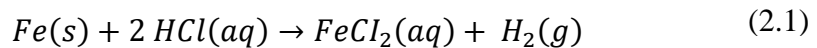
In this equation, the indices (s), (aq), and (g) refer to the solid, aqueous and gaseous phases respectively. In aqueous phase, hydrochloric acid and ferrous chloride exist in ionic form. Therefore, we can also write:

$$Fe + 2\ H^+(aq) + 2\ CI^-(aq) \rightarrow\ Fe^{2+}(aq) + 2\ CI^-(aq) +\ H_2(g) \quad (2.2)$$
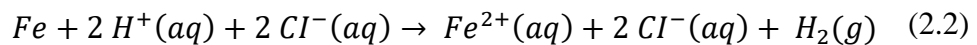
From this equation, the oxidizing agent is the solvated proton, $H^+(aq)$. The products of the reaction are the solvated ferrous ion, $Fe^{2+}(aq)$ and gaseous hydrogen, $H_2(g)$. The reaction (2.2) can also be expressed as follows because the chloride ions do not undergo a chemical change.

$$Fe + 2\ H^+ \rightarrow\ Fe^{2+} +\ H_2 \qquad (2.3)$$
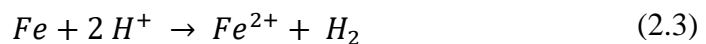
2.2.2.1 Partial Reaction

All redox reactions consist of two partial reactions, also sometimes called half-cell reactions. The partial oxidation reaction also referred to the anodic partial reaction and the partial reduction reaction or cathodic partial reaction. Thus for reaction (2.3):

Anodic partial reaction

$$Fe \rightarrow Fe^{2+} + 2\,e \qquad\qquad (2.4)$$

Cathodic partial reaction

$$2\,H^+ + 2\,e \rightarrow H_2 \qquad\qquad (2.5)$$

Overall reaction

$$Fe + 2\,H^+ \rightarrow Fe^{2+} + H_2 \qquad\qquad (2.6)$$
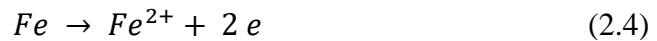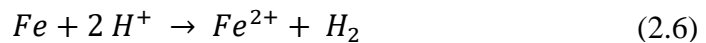
The anodic and cathodic partial reactions show explicitly the electrons that are exchanged during the course of the redox reaction.

Any chemical transformation that implies the transfer of charge across the interface between an electronic conductor (the electrode) and an ionic conductor (the electrolyte) is referred to as an electrochemical reaction.

The driving force for the movement of electron from mild steel to reducing species is the differences in the atom binding energies within the metal. Meanwhile, corrosion is also induced by the ion concentration gradients in the electrolyte. In corrosion process, water is the most common electrolyte for the transferring of ions and electrons since it present naturally in the environment.

2.2.3 Corrosion Mitigation Steps

Several mitigation steps have been introduced and applied in most of the chemical industries to reduce the impact of metal corrosion. Some commonly methods used are cathodic protection, protection with anticorrosive coating and corrosion inhibitors. These type of corrosion prevention are briefly described in Table 2.2

Table 2. 2   Types of corrosion prevention (Palou et al., 2014).

Type of corrosion prevention	Description
Cathodic protection.	An effective method to control corrosion on structures either buried or immersed in an electrolyte. It is a modification on the interfacial potential between metal surface and the medium where the metal is exposed to.
Protection with anticorrosive coating.	Used to form a physical barrier between the corrosive environments to protect the structure. It is used mainly with metallic elements exposed to the atmosphere. A passivation layer that coat on the metal surface to prevent the corrosive substance from contacting the metal surface.
Corrosion Inhibitors.	Substances that added in small concentrations (parts per million, ppm) to a corrosive environment and will be adsorbed either physically or chemically on the metal surface with the formation of protective layer to decrease the corrosion rate effectively.

Among these mitigations mentioned, the use of corrosion inhibitor is a popular technique to prevent the corrosion rate of metals in chemical environments (Jayakumar et al., 2014)

2.3   Corrosion Inhibitor

The use of corrosion inhibitors is the most economical and practical method in reducing corrosive attack on metals. Corrosion inhibitors are substances which when a small concentrations is added to corrosive media in order to decrease or prevent the reaction of the metal with the media (Raja and Sethuraman, 2008). Based on Otaibi et al. (2014), corrosion inhibitors are chemicals either synthetic or natural which, when added in small amounts to an environment, decrease the rate of attack by the environment on metals. However, due to the strict environmental regulations and toxic effects of synthetic compounds on human and animal life, the popularity and use of synthetic compounds as a corrosion inhibitor is diminish. Thus, the need to develop a new class of corrosion inhibitors with low toxicity, eco-friendliness and good efficiency is required.

Inhibitor reduce the corrosion rate by: (i) Increasing or decreasing the anodic and/or cathodic reaction (ii) decreasing the diffusion rate for reactants to the surface of the metal (iii) Decreasing the electrical resistance of the metal surface. Inhibitors are often easy to apply and offer the advantage of in-situ application without causing any significant disruption to the process (Raja and Sethuraman, 2008).

The application of surfactants as corrosion inhibitors has been extensively studied, and adsorption of the surfactant on the metal surface was found to be responsible for the corrosion inhibition of the metal surface. Most acid inhibitors are organic compounds containing nitrogen, sulphur and/or oxygen atoms. The inhibition mechanism is a separation process involving (i) the inhibitor is adsorbed on the surface of the metal forming a compact protective thin layer and (ii) the inhibitor forms a precipitate on the surface of the metal, acting on the aggressive media to form protective precipitates or remove the aggressive agents (Sayed et al., 2010).

2.3.1   Green Corrosion Inhibitor

Due to the toxic effects of synthetic or inorganic inhibitor, study of natural plants as green corrosion inhibitors are highly acceptable because these are eco-friendly, cheap, non-toxic and easily available. In recent days, many alternative eco-friendly corrosion inhibitors have been developed. Various parts of plants such as seeds, fruits, leaves, flowers, and etc. have been used as corrosion inhibitors (Sharmila et al., 2010). Plant materials contain proteins, polysaccharides, polycarboxylic acids and alkaloids. These compounds are potential acid corrosion inhibitors for many metals (Zucchi and Omar, 1985).

Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost and are biodegradable in the environment. Entering into the 21st century, along with people's increasing awareness of protecting the environment, a large number of researches about plant extracts as effective corrosion inhibitors of iron or steel in acidic media have been reported (Cang et al., 2013).

Through these studies, it is agreed that the inhibition performance of plant extract is normally ascribed to the presence in their composition of complex organic species such as tannins, alkaloids and nitrogen bases, carbohydrates, amino acids and proteins as well as hydrolysis products. These organic compounds contain polar functions with nitrogen, sulphur and oxygen atoms as well as conjugated double bonds or aromatic rings in their molecular structures, which are the major adsorption centers (Cang et al., 2013).

2.3.1.1 Green Corrosion Inhibition of Mild Steel in HCl Solution

Green corrosion inhibitors have continued to attract attention as replacement for synthetic organic inhibitors due to its relatively cheap, eco-friendly, nontoxic and readily available.

In this section, various types of natural corrosion inhibitors (plant extracts) that used to minimize the corrosion rate of mild steel in corrosive medium will be discussed. The type of plant extract, method used, adsorption isotherm and efficiency for each inhibitor are tabulated in Table 2.3.

According to the studies from the researches mentioned in the Table 2.3, it is noticed that the presence of heteroatoms such as nitrogen, sulphur, phosphorous and oxygen in the organic compound molecule improves its action as mild steel corrosion inhibitor. This is explained by the presence of vacant d orbitals in iron atom that form coordinative bonds with atoms able to donate electrons. Interaction with rings containing conjugated bonds, π electrons, is also present (Antonijevic and Petrovic, 2008) .These compounds get adsorbed onto the surface of metal from the bulk of environment forming a film at the metal surface. The inhibition efficiency increases in the order $O < N < S < P$ (Chetouani et al., 2002).

Table 2. 3   Plants extracts as corrosion inhibitors for mild steel

No	Corrosive Medium	Plant Extract	Methods	Effect of temperature on % inhibition efficiency	Effect of concentration on % inhibition efficiency	Adsorption Isotherm	Inhibition Efficiency (%)	Reference
1	HCl	*Pentaclethra Macrophylla Bentham*	Weight loss and EIS	Decrease	Increase	Langmuir and Temkin	95.6	(Nnanna et al., 2014)
2	HCl	*Lycium shawii*	EIS	Decrease	Increase	_	85.4	(Otaibi et al., 2014)
3	HCl	*Aloes*	Weight loss and EIS	Decrease	increase	Langmuir	77.00	(Cang et al., 2013)
4	H_2SO_4	*Citrus aurantium*	Weight loss	Decrease	Increase	Langmuir	89.00	(Hassan et al., 2016)
5	HCl	*Murraya koenigii*	Weight loss and Gasometric	Decrease	Increase	Langmuir	84.6	(Sharmila et al., 2010)
6	H_2SO_4	*Murraya koenigii*	Weight loss and EIS	Decrease	Increase	Langmuir	94.66	(Quraishi et al., 2010)
7	H_2SO_4	watermelon rind	EIS	Done at constant temperature	Increase	Temkin	77.34	(Odewunmi et al., 2015)
8	drinking water	*Acacia seyal var. seyal*	potentiodynamic polarization and EIS	Decrease	Increase	-	75.00	(Buchweishaija and Mhinzi, 2008)
9	HCl	*Aloe Vera*	Weight loss and EIS	Decrease	Increase	Langmuir	92.00	(Singh et al., 2016)
10	industrial water	*Pterolobium hexapetalum*	Weight loss and EIS	Decrease	Increase	Langmuir	75.76	(Kumar and Mohana, 2014)

Nnanna et al. (2014) have investigated the effect of *Pentaclethra macrophylla Bentham* root extracts for mild steel in 1M HCl medium. Weight loss and electrochemical impedance Spectroscopy were used in the investigation at 30°C - 45°C. The maximum inhibition efficiency was found to be around 95.6 %. Tannins, saponins, flavonoids, alkaloids and phenols are the active constituents in extract of *Pentaclethra macrophylla Bentham*. The presence of these active phytoconstituents in the extracts may have great influence on their corrosion inhibition property. The adsorption of these compounds on the mild steel surface obeys Langmuir's and Temkin's isotherm.

Buchweishaija and Mhinzi (2008) have studied the gum exudates from *Acacia seyal var. seyal* as an inhibitor for mild steel corrosion in drinking water systems. From this studied, the gum exudate is found to block the electrochemical processes taking place on the steel undergoing corrosion in water. It reduces both the rate of cathodic and anodic reactions by reducing the current densities on both sides of the polarization curves in the potential region studied and hence reduces the corrosion rate. This factor suggest that the *Acacia seyal var. seyal* inhibitor acts as anodic type corrosion inhibitor. The product was found to efficiently inhibit the corrosion of mild steel up to 75 %.

Singh et al. (2016) have analyzed the corrosion inhibition efficiencies of *Aloe Vera* gel as corrosion inhibitors of mild steel in 1 M HCl medium at different inhibitor concentration (0 ppm – 200 ppm), temperature (308 K – 338 K), immersion time (3 h – 168h) and acid concentration (0.5 M – 2.5 M) by using weight loss, electrochemical impedance spectroscopy (EIS), and Tafel polarization technique. From the experiment, the *Aloe Vera* extract was found to be a good inhibitor for mild steel corrosion in HCl with maximum efficiency up to 92 % and obeyed Langmuir

adsorption isotherm. Besides, the results obtained from weight loss, impedance and polarization studies are in a good agreement.

From the reviews, most of the inhibitor compounds obey the Langmuir adsorption isotherm on the mild steel surface except for the watermelon rind extract by Odewunmi et al. (2015), which follows Temkin adsorption isotherm and for the *Pentaclethra macrophylla Bentham* extract by Nnanna et al. (2014), its follow both of Langmuir and Temkin adsorption isotherm. This showed that there is formation of layer of insoluble complex of the metal on the surface which acts as a barrier between the mild steel surface and the corrosive medium. This protective film layer will avoid the corrosive substance from reaching the mild steel surface.

2.3.2 *Cymbopogon citratus* as a Green Inhibitor

C. citratus also known as lemongrass is a herb that grows in most tropical countries. It belongs to the genus Cymbopogon of aromatic grasses and contains essential oil with fine lemon flavor due to its high content of the aldehyde citral, which has two geometric isomers, geranial (citral a) and neral (citral b) (Shahi et al., 2005). These constituents contain π-bonds, and oxygen atoms in their molecular structures as active centers. The various chemical constituents present in the inhibitor solutions were synergized the inhibition effect of each other (Chaubey et al., 2015). Citral is also an important raw material used in the pharmaceutical, cosmetic and perfumery industries especially for the synthesis of ionone, which are important components in high class perfumery. Its chemical structure are shown in Figure 2.1 (macognogy, 2012).
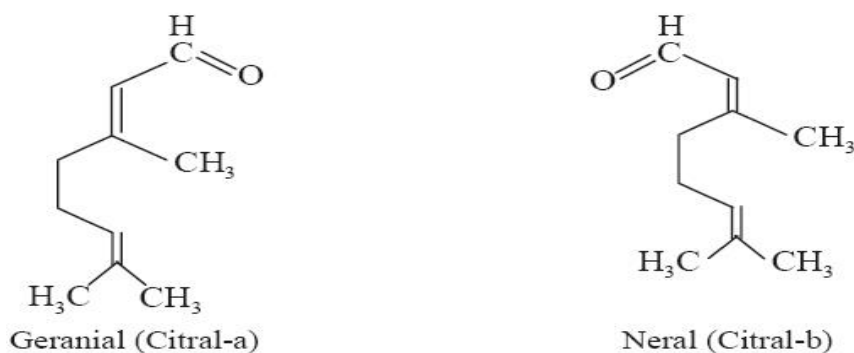

Figure 2. 1 Chemical constituents present in *C. citratus* leaves

2.4 Adsorption Inhibitor

The corrosion inhibition of a metal may involve either physisorption or chemisorption of the inhibitor on the metal surface (Godec, 2006). Physisorption involves electrostatic forces between ionic charges or dipoles on the adsorbed species and the electric charge at the metal/solution interface. If the heat of adsorption is low, thus, this adsorption is only stable at relatively low temperature. While chemisorption involves charge transfer or sharing from the inhibitor molecules to the metal surface to form a coordinate type bond. This type of adsorption is known to have much stronger adsorption energy compared to the other mode of adsorption. Thus, such bond is more stable at higher temperature (Kairi and Kassim, 2013).

2.5 Weight Loss Measurement

There are a few measures that can be performed to study the corrosion rate and the inhibition efficiency of mild steel in hydrochloric acid solution. Weight loss, Gravimetric analysis, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) are the common method used to study corrosion of metal. From these, weight loss measurement is the simplest, most common and longest-established method. However, the problem with this technique compared to other technique performed are longer time required to get the result and less accuracy due to human and instrumentation errors when weighing the specimen before and after the test.

Based on Iroha et al. (2015), weight loss can be calculated by determining the difference between the initial weight of the mild steel before immersion with the weight after the mild steel was retrieved from the corrosive environment. Thus,

$$\Delta W = W_{initial} - W_{final} \qquad\qquad (2.7)$$

Where, $W_{initial}$ is initial weight of the mild steel before immersion and W_{final} is weight after the mild steel was retrieved from the corrosive environment.

2.6 Inhibition Efficiency

By using the corrosion rate data calculated, the inhibition efficiency, % η_w and surface coverage, θ can be determined by using the following equation (Quraishi et al., 2010) :

$$\eta_w = \frac{Wo - Wi}{Wo} \, X \, 100 \qquad\qquad (2.8)$$

Where Wi and Wo are the weight loss value in presence and absence of inhibitor respectively. The high weight loss of mild steel indicates that the inhibition efficiency of corrosion inhibitor is low, and vice versa.

2.7 Corrosion Rate of Mild Steel

After obtaining the weight loss of mild steel, the corrosion rate, CR of the mild steel in HCI solution can be calculated using the equation below (Andreani et al., 2016) :

$$CR \left(\frac{mg}{cm^2.hr}\right) = \frac{\Delta W}{A_s t} \qquad\qquad (2.9)$$

Where,

$\Delta W = $ corrosion weight loss of mild steel (mg)

$A_s = $ area of the coupon (cm^2)

$t = $ exposure time (hr)

2.8 Adsorption Isotherm

In this section, three different adsorption isotherms are discussed. Isotherms explain the adsorption using the relationship between the amounts of adsorbate (inhibitor molecules) which is adsorbed on the adsorbent (surface of mild steel). The adsorption isotherms explored to determine the mode of adsorption of *C. Citratus* leaves extract inhibitor compound on the mild steel surface are the Langmuir, Temkin and Frumkin isotherms. These models are given respectively by Lebrini et al. (2011). The correlation coefficient, R^2 is used to determine the best fitting of the experimental data to the adsorption isotherms mentioned.

2.8.1 Langmuir Isotherm

Langmuir isotherm is based on assumption that all adsorption sites are equivalent and that particle binding occurs independently from nearby sites being occupied or not (Lebrini et al., 2011). Langmuir adsorption isotherm was used to deduce whether there is formation of layer of insoluble complex of the metal on the surface which acts as a barrier between the metal surface and the corrosive medium (usually termed physisorption). The linearized Langmuir isotherm equation that has been modified is given by:

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh} \qquad (2.10)$$

Where,

$C_{inh} =$ Concentration of inhibitor (g/L)

$\theta =$ Surface coverage

$K =$ Equilibrium constant of adsorption (L/g)

By plotting a graph of $\frac{C_{inh}}{\theta}$ against C_{inh} , the value of K can be determined from the y-intercept value of the plot.

2.8.2 Frumkin Isotherm

The linearized Frumkin isotherm equation that has been modified is given by:

$$\ln\left[C_{inh}\left(\frac{1-\theta}{\theta}\right)\right] = \log K + 2a\theta \qquad (2.11)$$

Where,

$C_{inh} =$ Concentration of inhibitor $\left(\frac{g}{L}\right)$

$\theta =$ Surface coverage

$K =$ Equilibrium constant of adsorption (L/g)

$a =$ Interaction parameter (the value can either be positive or negative)

By plotting a graph of $\ln\left[C_{inh}\left(\frac{1-\theta}{\theta}\right)\right]$ against θ , the value of K and a can be determined from the y-intercept and slope values of the plot, respectively.

2.8.3 Temkin Isotherm

Temkin isotherm was used to determine if the extract adsorption on the metal surface is via chemisorption which involves displacement of water molecules from the metal surface and the sharing of electrons between oxygen atom and iron.

The linearized Tamkin isotherm equation that has been modified is given by:

$$\theta = -\frac{1}{2a}\ln K - \frac{1}{2a}\ln C_{inh} \qquad (2.12)$$

Where,

$C_{inh} =$ Concentration of inhibitor $\left(\dfrac{g}{L}\right)$

$\theta =$ Surface coverage

$K =$ Equilibrium constant of adsorption (L/g)

By plotting a graph of θ against C_{inh} , the value of K and a can be determined from the y-intercept and slope values of the plot, respectively.

2.9 Kinetic Parameters of Activation.

Thermodynamic parameters are important to study the inhibitive mechanism. A kinetic model was another useful tool to explain the mechanism of corrosion inhibition for the inhibitor. The logarithm of the corrosion rate (CR) could be represented as a straight line function of 1/T of mild steel in acid medium:

$$\ln CR = \frac{-E_a}{RT} + \ln A \qquad (2.13)$$

Where,

$E_a =$ apparent activation energy

$R =$ universal gas constant

$T =$ absolute temperature

$A = \text{pre} - \text{exponential factor}$

By plotting the graph of $\ln CR$ against 1/T, the slope of the graph can be used to determine the E_a while the y-intercept can be used to determine the value of A.

2.10   Thermodynamics and Kinetics Studies

Thermodynamic model is very useful to explain the adsorption phenomenon of inhibitor molecule.

The adsorption heat could be calculated according to the Van't Hoff equation (Zarrouk et al., 2011)

$$\ln K_{Ads} = -\frac{\Delta H^{\circ}_{Ads}}{RT} + constant \tag{2.14}$$

Where ΔH°_{Ads} and K_{Ads} are the adsorption heat and adsorptive equilibrium constant, respectively. To obtain the adsorption heat, the graph of lnK_{Ads} against 1/T was plotted. The constant of adsorption,K_{Ads} is related to the standard free energy of adsorption, ΔG°_{Ads} from the following equation:

$$K_{Ads} = \frac{1}{55.55} \exp\left(\frac{-\Delta G^{\circ}_{Ads}}{RT}\right) \tag{2.15}$$

Where R is the universal gas constant and T is the absolute temperature. The value 55.55 in the above equation is the concentration of water in solution in mol L^{-1}.

The standard adsorption entropy ΔS°_{Ads} may be deduced using the thermodynamic basic equation:

$$\Delta G^{\circ}_{Ads} = \Delta H^{\circ}_{Ads} - T\Delta S^{\circ}_{Ads} \tag{2.16}$$

The spontaneity of corrosion of metal (Table 2.4) can be determined by the positive or negative value of ΔG°_{Ads} obtained. Since the corrosion of mild steel involved species of two different phases, the following explanation can be used to explain the spontaneity of the reaction.