

**INHIBITIVE ACTION OF *MORINGA OLEIFERA* SEED POD
EXTRACT FOR THE CORROSION OF ALUMINIUM IN 1.0 M
HYDROCHLORIC ACID (HCl) SOLUTION**

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UNIVERSITI SAINS MALAYSIA

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HYDROCHLORIC ACID (HCl) SOLUTION**

by

KISHEELAH A/P RAKAVAN

**Thesis submitted in partial fulfilment of the requirement for the
degree of Bachelor of Chemical Engineering**

June 2018

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
LIST OF SYMBOL	ix
LIST OF ABBREVIATIONS	xi
ABSTRAK	xii
ABSTRACT	xiv
CHAPTER ONE: INTRODUCTION	1
1.1 Research Background	1
1.2 Problem Statement	4
1.3 Research Objectives	5
1.4 Research Scope	5
CHAPTER TWO: LITERATURE REVIEW	7
2.1 Overview of Corrosion	7
2.2 Corrosion of Metals	8
2.3 Corrosion of Aluminium (Al) in corrosive (acidic/alkaline) medium	11
2.4 Principles, Mechanisms and Applications of Corrosion Inhibitors	13
2.5 Plant extract as a potential green corrosion inhibitor	18
2.6 Method of Extraction for Natural Products	20
2.7 <i>Moringa oleifera</i> extract as a potential green corrosion inhibitor	22
2.8 Parameters Studied on Corrosion Inhibition of Aluminium	23

2.8.1 Effect of concentration of corrosion inhibitor	23
2.8.2 Effect of temperature of corrosion inhibitor	23
2.8.3 Effect of period of immersion	24
2.9 Adsorption Isotherm and Kinetic Studies of <i>Moringa oleifera</i>	24
2.10 Thermodynamic Aspects Involved in Corrosion Inhibition	27
CHAPTER THREE: MATERIALS AND METHOD	29
3.1 Materials and Chemicals Required	30
3.2 Equipment and Facilities Required	30
3.3 Extraction from <i>Moringa oleifera</i> seed pod	31
3.3.1 Preparation method	31
3.3.2 Extraction method using ultrasonicator	32
3.4 Preparation of aluminium plates and test solution	35
3.5 Preparation of corrosion inhibitor stock solution	36
3.6 Corrosion inhibition using different concentrations of <i>Moringa oleifera</i> seed pod extract	36
3.7 Corrosion inhibition using different temperatures of 1.0 M HCl solution	38
3.8 Characterization study of <i>Moringa oleifera</i> seed pod extract	38
3.9 Adsorption Mechanism and Isotherm of Corrosion Inhibition by <i>Moringa oleifera</i> seed pod extract	39
3.9.1 Langmuir isotherm	40
3.9.2 Freundlich isotherm	40
3.9.3 Temkin isotherm	41
3.9.4 El-Awady and Ahmad isotherm	41
3.10 Thermodynamic Aspects of Corrosion Inhibition of Aluminium Plates	41

CHAPTER FOUR: RESULTS AND DISCUSSION	44
4.1 Characterization of <i>Moringa oleifera</i> seed pod extract	44
4.1.1 Gas Chromatography Mass Spectrometry (GCMS)	44
4.1.2 Fourier Transform Infrared Spectroscopy (FTIR)	46
4.2 Corrosion inhibition studies	49
4.2.1 Effect of inhibitor concentration on Al corrosion at a constant HCl concentration (1.0 M)	49
4.2.2 Effect of temperature on Al corrosion at 1.0 M HCl using optimum inhibitor concentration (1.8g/L)	51
4.3 Adsorption Mechanism and Isotherm of Corrosion Inhibition by <i>Moringa oleifera</i> seed pod extract	53
4.4 Thermodynamic Aspects of Corrosion Inhibition of Aluminium Plates	54
CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS	59
5.1 Conclusion	59
5.2 Recommendations	60
REFERENCES	61
APPENDIX	70

LIST OF TABLES

		Page
Table 1.1	Wrought Aluminium and Aluminium Alloy Designation	2
Table 2.1	Forms of Corrosion and Its Description	9
Table 2.2	Green corrosion inhibitor used in researches for aluminium and its alloy in acid or alkaline solution	20
Table 2.3	Examples of several adsorption isotherm model	26
Table 3.1	List of materials and chemicals	30
Table 3.2	List of equipment and facilities	30
Table 4.1	Chemical compounds found in <i>M. oleifera</i> seed pod extract by using GCMS	46
Table 4.2	Peaks of adsorption from FTIR spectra of aluminium after weight loss studies	48
Table 4.3	The studied adsorption isotherm models	53
Table 4.4	The values of thermodynamic parameters E_a , ΔH^* and ΔS^* for aluminium plates in 1.0 M HCl in the absence and presence of optimum concentration of <i>M. oleifera</i> seed pod extract	57

LIST OF FIGURES

		Page
Figure 2.1	Classification of Inhibitors	15
Figure 2.2	Illustration of anodic inorganic inhibitors effect and their mechanism of action	16
Figure 2.3	Mechanism of action of cathodic inhibitors	16
Figure 2.4	Mechanism of actuation of organic inhibitor	17
Figure 2.5	Market Demand of Inhibitors in 2012	18
Figure 3.1	Research flow diagram	29
Figure 3.2	Ground <i>M. oleifera</i> seed pods	32
Figure 3.3	Grinder	32
Figure 3.4	Sieved plant material	32
Figure 3.5	Sieve shaker	32
Figure 3.6	Ethanol (aq) in containers	33
Figure 3.7	Six containers mixed with ethanol (aq) and sieved powder	33
Figure 3.8	Ultrasonicator	33
Figure 3.9	Arrangements of six containers in ultrasonicator	33
Figure 3.10	Extracted samples after sonication	34
Figure 3.11	Centrifuge	34
Figure 3.12	Centrifuge tube containing extracted sample	34
Figure 3.13	Rotary evaporator under vacuum	35
Figure 3.14	Formation of thick semisolid residue after evaporation	35
Figure 3.15	Experiment set up for corrosion inhibition studies varying the inhibitor concentration	36

Figure 3.16	Weighing process of aluminium before they were immersed in the HCl acid solution	37
Figure 3.17	Fourier Transform Infrared Spectroscopy (FTIR)	39
Figure 4.1	GCMS spectrum for pure <i>M. oleifera</i> seed pod extract	45
Figure 4.2	FTIR result of aluminium surface before and after corrosion	47
Figure 4.3	Effect of inhibitor concentration on percentage of inhibition efficiency at 298 K with immersion time of 2 hours	50
Figure 4.4	Effect of temperature on inhibitor efficiency in 1.0 M HCl at optimum inhibitor concentration (1.8g/L) with immersion time of 2 hours	52
Figure 4.5	Langmuir's isotherm plot for adsorption of inhibitors on the surface of aluminium in 1.0 M HCl solution	54
Figure 4.6	Arrhenius plots of $\log C_R$ versus $1/T$ for aluminium in 1.0 M HCl in the absence and presence of 1.8g/L <i>M. oleifera</i> seed pod extract as corrosion inhibitor	55
Figure 4.7	Adsorption isotherm plots of graph against $\log (C_R/T)$ and $1/T$ used for determining the activation parameters	56

LIST OF SYMBOL

	Symbol	Unit
A	Area of aluminium plates	cm ²
Al	Aluminium plates	-
C _R	Corrosion rate	mm/y
C _{inh}	Inhibitor concentration	g/L
E _a	Arrhenius activation energy of adsorption	kJ/mol
ΔG ^o _{ads}	Free energy of adsorption	kJ/mol
h	Planck's constant	6.626×10 ⁻³⁴ J/s
ΔH*	Enthalpy of activation	kJ/mol
HCl	Hydrochloric acid	-
K _{ads}	Adsorption equilibrium constant	L/g
K _L	Langmuir adsorption constant	L/g
K _T	Temkin adsorption constant	-
K _F	Freundlich adsorption constant	-
N	Avogadro's number	6.02×10 ²³
R	Universal gas constant	8.314 J/mol.K
R ²	Correlation coefficient	-
ΔS*	Entropy of activation	J/K.mol
t	Exposure/ Immersion time	h
T	Temperature	K
ω _o	Weight loss in the absence of inhibitors	g
ω _i	Weight loss in the presence of inhibitors	g
ΔW	Weight loss	mg

η	Percentage inhibition efficiency	%
θ	Surface coverage	-
ρ	Density of aluminium plates	g/cm^3

LIST OF ABBREVIATIONS

FTIR	Fourier Transform Infrared Spectroscopy
GCMS	Gas Chromatography Mass Spectrometry
<i>M. oleifera</i>	<i>Moringa oleifera</i>

**PENGGUNAAN EKSTRAK POD BENIH *MORINGA OLEIFERA* SEBAGAI
PERENCAT KAKISAN UNTUK ALUMINIUM DALAM 1.0 M LARUTAN ASID
HIDROKLORIK**

ABSTRAK

Aluminium adalah salah satu logam yang kerap digunakan dalam industri pembinaan, aeroangkasa, mekanikal, kimia dan sebagainya. Namun begitu, aluminium menunjukkan sifat kekakisannya apabila didedahkan kepada bahantara agresif seperti media yang sangat berasid atau beralkali. Terdapat pelbagai cara yang diteroka untuk mencegah kakisan aluminium dalam bahantara agresif. Antara cara yang mesra alam untuk merencat kakisan aluminium adalah menggunakan produk semulajadi iaitu ekstrak dari tumbuh-tumbuhan. Dalam kajian ini, pencegahan kakisan aluminium dalam 1.0 M larutan asid hidroklorik (HCl) dengan ekstrak pod benih *Moringa oleifera* telah dikaji dengan menggunakan kaedah penurunan berat. Kajian ini menunjukkan bahawa peratusan kecekapan perencatan meningkat dengan peningkatan kepekatan ekstrak. Ekstrak pod benih *M. oleifera* mempamerkan kecekapan perencatan, η (%) yang maksima sebanyak 96.4 % pada 1.8 g/L dalam suhu bilik (289K) yang merupakan kepekatan ekstrak yang optimum. Selain itu, kesan suhu ke atas tingkah laku kakisan aluminium dalam 1.0 M HCl dengan penambahan kepekatan ekstrak optimum juga dikaji. Hasil kajian ini mendedahkan bahawa peratusan kecekapan perencatan menurun dengan peningkatan suhu dari 303K hingga 343K. Filem terjerap pada permukaan aluminium yang mengandungi *M. oleifera* daun ekstrak juga diukur oleh Kromatografi Gas – Spektrometri Jisim (GCMS) dan Spektroskopi Transformasi Fourier Infra Merah (FTIR). Keputusan yang diperolehi menunjukkan bahawa sebatian yang bertanggungjawab bagi perencatan kakisan ialah sebatian asid lemak. Tambahan pula, penjerapan ekstrak pod benih *M.*

oleifera di atas permukaan aluminium mematuhi isoterma penjerapan Langmuir. Parameter termodinamik untuk proses perencatan tersebut seperti tenaga pengaktifan bagi penjerapan (E_a), entalpi (ΔH^*) dan entropi (ΔS^*) pengaktifan, tenaga bebas Gibbs (ΔG°_{ads}) telah dikira and dianalisiskan. Nilai E_a , ΔH^* , ΔS^* dan ΔG°_{ads} yang diperolehi adalah 101.27 kJ/mol, 98.63 kJ/mol, 101.48 kJ/mol dan -19.01 kJ/mol masing-masing. Nilai tersebut menunjukkan bahawa proses penjerapan ini adalah tindak balas serap haba, spontan dan molekul perencat telah terjerap di atas permukaan aluminium melalui penjerapan fizikal. Dengan ini, kajian ini membuktikan bahawa ekstrak pod benih *M. oleifera* boleh menjadi perencat berkesan daripada kakisan aluminium dalam media larutan asid hidroklorik.

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THE CORROSION OF ALUMINIUM IN 1.0 M HYDROCHLORIC ACID (HCl)
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ABSTRACT

Aluminium is most widely used metal after iron in the industries like construction, aerospace, chemical, mechanical and others. However, it showed corrosion behaviour in aggressive environments such as highly acidic or alkaline media. There are numerous methods that have been explored to prevent corrosion of aluminium in aggressive media. One of the most environmental friendly methods is using natural products like plant extracts to inhibit corrosion. In this research study, the inhibitive action of *M. oleifera* seed pod extract on aluminium corrosion in 1.0 M hydrochloric acid (HCl) solution was studied using weight loss technique. The percentage of inhibition efficiency was found to be increasing with the increasing inhibitor concentration. *M. oleifera* seed pod extract exhibited the maximum inhibition efficiency, η (%) of 96.4% at 1.8g/L (optimum concentration) under room temperature (289 K). The effect of temperature on the corrosion behaviour of aluminium in HCl solution with addition of optimum extract concentration was also studied. The result revealed that the percentage of inhibition efficiency decreases as the temperature increases in the range of 303 K – 343 K. The characterization study of *M. oleifera* seed pod extract was carried out using Gas Chromatography Mass Spectrometry (GCMS) and Fourier Transform Infrared Spectroscopy (FTIR). The results depicts that the compound responsible for the inhibitive action is fatty acid compounds. In addition, the inhibition occurred via adsorption of the inhibitor molecules on the aluminium surface obeying the Langmuir adsorption isotherm. Besides, thermodynamic parameters such as activation energy (E_a), enthalpy (ΔH^*) and

entropy (ΔS^*) of activation for corrosion process as well as free energy of adsorption value ($\Delta G^{\circ}_{\text{ads}}$) were calculated and discussed. The value of E_a , ΔH^* and ΔS^* and $\Delta G^{\circ}_{\text{ads}}$ obtained in the presence of inhibitor was 101.27 kJ/mol, 98.63 kJ/mol, 101.48 kJ/mol and -19.01 kJ/mol respectively. These calculated values revealed that the adsorption process are endothermic, spontaneous and the inhibitor molecules were adsorbed on the aluminium surface through physisorption. Thus, it can be concluded that the seed pod extract of *M. oleifera* could serve as an effective inhibitor of the corrosion of aluminium in HCl solution.

CHAPTER ONE

INTRODUCTION

1.1 Research Background

Corrosion inhibition of metals has become a daily process in industries since they depend heavily on the use of metals and its alloys (Al-Otaibi et al., 2014). Metals and its alloys react chemically or electrochemically with corrosive medium (acidic or alkaline) to form stable compound in which the metals become corroded. Deterioration of metal's surface when it is reacted with the corrosive medium is called corrosion (Bell, 2017). For this research, corrosion of aluminium has been studied in the highly concentrated acidic medium. Aluminium is one of the most prevalent metallic elements in the solid portion of earth's crust, comprising approximately 8% (Hussain, 2015). It is always found in combined form, normally as hydrated oxide, of which bauxite is the primary ore (Hussain, 2015). Basically, aluminium and its alloys are classified based on the major alloying element via a four-digit designation (XXXX). The first digit depicts the purity or alloy type. The second digit indicates modifications of the alloy; whereas in the 1XXX series only the third and fourth digit shows the purity. Table 1.1 below has clearly described the aluminium alloys designation.

Aluminium is also the most widely used type of metal after iron (Aisha et al., 2017). Aluminium and its alloys have been widely used in various applications such as automotive, aerospace, construction and electrical power generation because of its properties such as low cost, light weight, high thermal and electrical conductivity and good corrosion resistance inhibition (Chaubey et al., 2017a). Generally, aluminium has resistance to corrosion due to the formation of coherent surface oxide which impedes further reaction of aluminium with the environment. Therefore, aluminium and its alloys are also widely used in reaction vessels, pipes, machinery and chemical batteries.

Table 1.1: Wrought Aluminium and Aluminium Alloy Designation (Hussain, 2015)

Series Designation	Alloying Materials
1XXX	99.9% min Al
2XXX	Al-Cu, Al-Cu-Mg, Al-Cu-Mg-Li, Al-Cu-Mg-Si
3XXX	Al-Mn, Al-Mn-Mg
4XXX	Al-Si
5XXX	Al-Mg, Al-Mg-Mn
6XXX	Al-Mg-Si, Al-Mg-Si-Mn, Al-Mg-Si-Cu
7XXX	Al-Zn, Al-Zn-Mg, Al-Zn-Mg-Mn, Al-Zn-Mg-Cu

HCl solutions are used for pickling, chemical and electrochemical etching of aluminium (Metikoš-Huković et al., 2002). However, the presence of aggressive ions like chloride creates extensive localized attack (El-Etre, 2003). Various mechanisms have been proposed to explain the breakdown of the oxide film (Errata et al., 1994). One of them takes into account the adsorption of chloride ions on the oxide surface, penetration of chloride ions through the oxide film, and localized dissolution of aluminium at the metal/oxide interface in consecutive one-electron transfer reactions. Recently, research has shown that chloride does not enter the oxide film but it is chemisorbed onto the oxide surface and acts as a reaction partner, aiding dissolution via the formation of oxide–chloride complexes (Bogar and Foley, 1972).

In order to prevent corrosion, synthetic organic compounds are widely used as corrosion inhibitors. Because of their hazardous nature, researchers focus their attention on developing environmental friendly natural products of plants origin as corrosion inhibitors. Plant extracts have become important because they are environmentally acceptable, inexpensive, readily available and renewable sources of materials (Rani and

Bharathi, 2012). Extracts of plant material containing nitrogen, oxygen and /or sulphur atoms have been used to control the corrosion of aluminium and other metals in different acidic corrosion medium such as hydrochloric acid, sulphuric acid and more. Recent studies also estimated that United States demand for corrosion inhibitors will rise 4.1% per year which is equivalent to USD\$ 2.5 billion in 2017. This has proven that importance of corrosion inhibitors in industries especially natural products (Dariva and Galio, 2014).

In recent years, numerous researches have been carried out on inhibitive action of plant extracts for corrosion of metals. One of them is inhibition efficiency of *Palisota hirsute* extract on corrosion of aluminium in alkaline (KOH) solutions (Nnanna et al., 2014). Other than that, inhibitive effect of aloe vera gel on corrosion of mild steel in 1.0 M of HCl has been studied using weight loss method, electrochemical impedance spectroscopy and Tafel polarization (Singh et al., 2016b). This aloe vera gel has showed more than 90% inhibition efficiency on corrosion of mild steel in HCl solution. Moreover, the corrosion inhibition characteristics of *Hunteria umbellata* seed husk extracts on mild steel immersed in 1 M HCl and H₂SO₄ solutions were studied using weight loss method (Alaneme et al., 2016). There have been lots of corrosion inhibitors like extracts of papaya leaves, *Hibiscus sabdariffa* leaves, watermelon rind and so on. which were tested to inhibit corrosion of mild steel (Chigondo and Chigondo, 2016). However, minimal amount of studies were carried out on corrosion of aluminium (Chaubey et al., 2017b). Thus, this research is mainly aimed for corrosion of aluminium.

For this study, the inhibition efficiency of *M. oleifera* seed pod extract will be investigated. *M. oleifera*, also known as drumstick tree is a highly valued plant, distributed in many countries of the tropics and subtropics. It is the only genus in *Moringaceae* family and has an impressive range of medicinal uses with high nutritional value. Moreover, it is abundant and easily accessible in our country. In this study, the

inhibitory action of the seed pod extract of *M. oleifera* on the corrosion of aluminium in 1.0 M HCl solution will be investigated by varying the concentration of the extract and also reaction temperatures using weight loss method (James and Akaranta, 2009).

1.2 Problem Statement

A study has proven that, corrosion-related costs constitutes few percentage of the gross domestic product (GDP) of the most developed countries in the world,¹ which sometimes can be on par with expenses for public education or healthcare (Xhanari et al., 2017) . This is a huge disadvantage, therefore corrosion and its related phenomena has to be given serious concern. In order to mitigate corrosion, several methods has been commercialised. One of the economical, practical and convenient methods to combat corrosion is using corrosion inhibitor. As mentioned earlier, highly toxic synthetic materials which contain compounds like arsenic, chromate and phosphorus were widely used as corrosion inhibitors in industries. There are also organic inhibitors like benzotriazole (BTA) and its derivatives which are excellent in inhibiting corrosion of mild steel and its alloys in wide ranges of media (Murthy and Vijayaragavan, 2014). However, they are really toxic and need to be replaced with eco-friendly inhibitors.

In the search of biodegradable inhibitors, natural products like plant extracts were fully utilised to prevent corrosion of metals. The results was really satisfactory where some of the plant extracts have showed maximum inhibition efficiency up to 90%. By using natural products which consist of bioactive compounds like phenolic acids and derivatives, corrosion can be prevented with highest efficiency as well as it does not impose any hazards to environment and health of community. Generally, corrosion of mild steel has been very popular now and studies on inhibitive action of plant extracts on mild steel were carried out abundantly. As we discuss about corrosion of aluminium,

limited amount of resources are present and more importance has to be given on inhibitive action of plant extracts on corrosion of aluminium in alkaline or acidic media. This is because the global production of aluminium is increasing each year whereby in September 2017 about 4,927,000 metric tons of aluminium were produced (Kelechava, 2017). The industry's growth is driven by rising China's output, which produced a whopping 2,606,000 metric tons of aluminium in September 2017, accounting for over half the total production. Thus, the growing annual production of aluminium creates a necessity to explore about corrosion inhibition of aluminium by using plant extracts as they are environmental friendly and safe to community.

1.3 Research Objectives

The objectives of this research project are:

1. To identify the functional composition of *M. oleifera* seed pod extract using Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography Mass Spectrometry (GCMS) equipment.
2. To study the effect of different concentrations of *M. oleifera seed pod* extract and different reaction temperature on the percentage of corrosion inhibition efficiency.
3. To investigate the adsorption mechanism, the isotherm of corrosion inhibition by *M. oleifera* seed pod extract on the aluminium surface and the thermodynamic aspects that are involved in the corrosion inhibition of the aluminium plates.

1.4 Research Scope

In this work, *M. oleifera* seed pod extract was utilised to inhibit corrosion of aluminium. The preparation of *M. oleifera* seed pod for extraction was done via physical method which applies cutting into small pieces, drying, grinding and sieving to enhance

the extraction yield. The powder was used for extraction by using ultrasonicator. The functional groups and compounds which were extracted from *M. oleifera* seed pod was tested and determined in Gas Chromatography Mass Spectrometry (GCMS) and Fourier Transform Infrared Spectroscopy (FTIR).

There were two parameters of the inhibitor studied which are the concentration of corrosion inhibitor and reaction temperature. First, the extracted compounds were added to 1.0 M HCl solution according the concentration stated in materials and method with aluminium plate immersed in it. By carrying out this experiment, the optimum concentration of inhibitor extract was determined by weight loss method. Then, the reaction temperature were manipulated and the results were obtained and analysed.

Then, the several adsorption isotherm were plotted to describe the effectiveness of the active compounds as corrosion inhibitor according to concentration of corrosion inhibitor and the degree of surface coverage. Among the isotherm plot, the best fitted line was chosen based on the value of the correlation coefficient (R^2) which is nearer to 1. Other than that, the thermodynamic parameters which are the activation energy (E_a), enthalpy (ΔH^*) and entropy (ΔS^*) of activation as well as free energy of adsorption value (ΔG°_{ads}) were calculated and analysed.

CHAPTER TWO

LITERATURE REVIEW

Chapter two briefly presents the previous discoveries and reviews available from credible scientific records and references that are related to this research topic. In general, this chapter outlines the overall review on corrosion of metals, narrowing down to corrosion of aluminium. Then, a detailed review on importance of corrosion inhibitors as well as plant extract emerging as a potential green corrosion inhibitor was also presented. At the same time, potential of *M. oleifera* as corrosion inhibitor and method of extraction was also discussed. Other than that, the parameters affecting the efficiency of corrosion inhibitor were explained. The kinetic studies and adsorption isotherm as well as thermodynamics involved in corrosion studies were also reviewed.

2.1 Overview of Corrosion




Corrosion is defined as chemical degradation of materials such as metals, semiconductors, insulators and even polymers, due to exposure to environment (Marcus, 2002). Degradation can also be referred as deterioration of physical properties of the particular material. It can be weakening of the material due to a loss of cross-sectional area, shattering of a metal due to hydrogen embrittlement or cracking of a polymer due to sunlight exposure. In addition, the fundamental cause or driving force for all corrosion is considered to be the lowering of system's Gibbs energy (Shaw and Kelly, 2006). Corrosion process develop rapidly after the disruption of the protective barrier and accompanied by several reaction which alters the composition and properties of both the metal surface and the local environment.

2.2 Corrosion of Metals

In general, most of the industries today depend heavily on the use of metals and alloys for multiple uses and applications. Examples of metals are mild steel, aluminium, stainless steel, copper, zinc, iron and so on. Since metals are the most used type of structural materials, corrosion control of metals is of technical, economic, environmental, and aesthetical importance (Rani and Bharathi, 2012). In addition, corrosion of metals play a major role in contributing numerous losses in industrial scope and have caused major accidents in industry. In 1995, an explosion was occurred at the Gaylord Chemical Corporation plant in Bogalusa, Louisiana due to corrosion through processing chemicals. The cause of this incident is leakage of large reddish-brown vapour due to corrosion and the vapour was eventually released from the tank. Therefore, prevention of corrosion of metals is really vital in industries to avoid any unforeseen incidents to take place.

Basically, corrosion of metals can be distinguished into different categories based on the material, environment or the morphology of the damage. There are many forms of corrosion and some of them are summarised in the Table 2.1. For corrosion of metals in corrosive media, pure metals and alloys react chemically or electrochemically with corrosive media which is also called as aggressive environments causing the metals surface to be corroded. Corrosion in the corrosive medium involves the movement of metal ions into the solution at active areas (anode), passage of electrons from the metal to an acceptor at less active areas (cathode), an ionic current in the solution and an electronic current in the metal (Raja and Sethuraman, 2008).

Table 2.1: Forms of Corrosion and Its Description (Heiney, 2018)

Forms of Corrosion	Description
 <p data-bbox="491 705 742 739">Uniform Corrosion</p>	<ul data-bbox="1029 336 1396 750" style="list-style-type: none"> • Also known as general corrosion. • The surface effect produced by most direct chemical attacks (e.g., as by an acid) is a uniform etching of the metal.
 <p data-bbox="475 1232 726 1265">Galvanic Corrosion</p>	<ul data-bbox="1029 828 1396 1243" style="list-style-type: none"> • An electrochemical action of two dissimilar metals in the presence of an electrolyte and electron conductive path. • Occurs when dissimilar metals are in contact.
 <p data-bbox="422 1747 805 1780">Concentration Cell Corrosion</p>	<ul data-bbox="1029 1321 1396 1848" style="list-style-type: none"> • Occurs when the surface of the metals are in contact with different concentrations of the same solution. • There are three types; metal ion concentration cell, oxygen concentration cells and active- passive cells.

Continued.



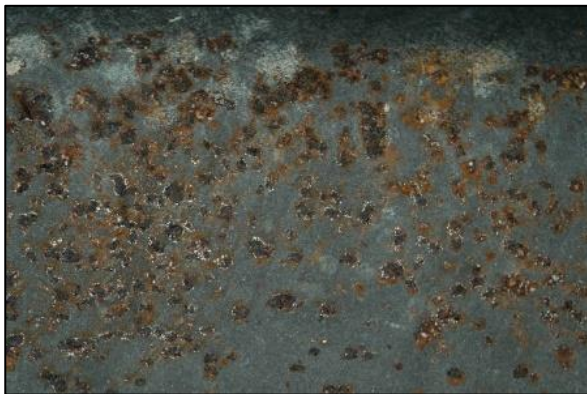
Filiform Corrosion

- Occurs on painted or plated surfaces when water breaches through the coating.
- Normally starts at small defects in the coating which spreads to cause structural weakness.



Erosion Corrosion

- Occurs when there is a combination of aggressive environment with high fluid-surface velocities.



Pitting Corrosion

- Localised corrosion caused by microscopic defects on metal surface.
- The pits are normally found underneath surface deposits due to corrosion product accumulation.

Continued.



Crevice Corrosion

- Produced at the contact region of metals with metals or metals with non-metals.

2.3 Corrosion of Aluminium (Al) in corrosive (acidic/alkaline) medium

Aluminium has long-established in numerous industries because of its good corrosion resistance behaviour. Moreover, aluminium is the second most used metal after iron because of its characteristics below (Azom, 2002):

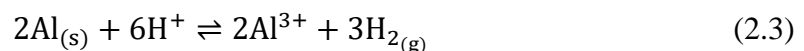
- i. Cheap
- ii. High thermal and electrical conductivity
- iii. Lighter
- iv. Low atomic mass
- v. High energy density

Aluminium is widely used in ship hulls, piers, tank interiors, offshore structure, submerged pipelines, piling and a lot more (Musa et al., 2011, Oguzie, 2007). From the research, it has been discovered that aluminium is dependent on the presence of inartificial film of surface oxides to resist from high corrosion. However, it showed a corrosion behaviour in aggressive environment. Examples of aggressive environment are highly acidic or alkaline media. Since aluminium is amphoteric, they dissolve substantially in high concentration acids or bases. This corrosive medium is responsible to reduce the oxide layer on the surface.

For acidic medium, HCl is normally used for pickling of aluminium and also for its chemical and electrochemical etching in which loss of metal occurs (corrosion) (Nnanna et al., 2011a). Corrosion of aluminium occurs due to the presence of aggressive ions in HCl like chloride, where it prevents the formation of the passive film and accelerates the process of anodic dissolution (Branzoi et al., 2003). Suitable mechanisms have been proposed to express the electrochemical process resulting from dissolution of aluminium in the acid. This process can be expressed by the anodic (oxidation) and cathodic (reduction) processes, which are defined by Equations (2.1) and (2.2) respectively,

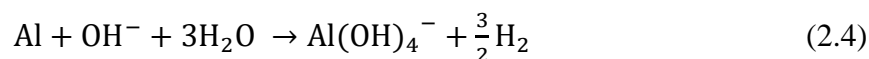


The overall electrochemical process can be written as follows:



There are some researches regarding the electrochemical behaviour of aluminium in different aqueous solutions, particularly regarding pitting corrosion due to the presence of chloride ions (Cabot et al., 1991, Szklarska-Smialowska, 1992, Beck, 1988, Ambat and Dwarakadasa, 1994, Bogar and Foley, 1972). The cause of the pitting corrosion of Al is the migration of chloride ions through the oxide film or due to the chemisorbed chloride ions onto the oxide surface where they act like reaction partners, aiding dissolution via the formation of oxide–chloride complexes (Branzoi et al., 2003).

On the other hand, it was also observed that alkaline solutions play a major role in reducing the oxide film. This is due to the fact that the protective oxide is dissolved by the OH^- ion and the surface of Al develops a negative potential. So, aluminium when exposed to highly concentrated alkaline solutions, the OH^- ions dissolves the oxide layer and the aluminium develops negative potential (Abiola and Otaigbe, 2008). The Equation (2.3) for this reaction is as follows (Aisha et al., 2017):



Furthermore, the study of aluminium corrosion in alkaline medium has been attracting considerable attention because of the numerous applications of this metal especially in aluminium (Al)/ air batteries. Al/air batteries are primary cells which capable of producing electricity from the reaction of oxygen in air with aluminium. They have higher energy densities compared to other batteries and also environmental friendly. However, it has not been commercialised due to severe hydrogen evolution problems resulting from corrosion of aluminium electrode (Aisha et al., 2017). This is because surface of Al corrodes or oxidises in alkaline solutions due to generating hydrogen molecules and other soluble species like $\text{Al}(\text{OH})_4^-$. Thus, certain control procedures has to be taken on hydrogen gas evolution without compromising the eco-friendly nature of the system, if the aluminium/air batteries need to be commercialised.

2.4 Principles, Mechanism and Applications of Corrosion Inhibitors

Protection of metals is such a challenging task yet much crucial matter in industrial scope. The use of inhibitors is one of the best options of protecting metals and alloys against corrosion (Rani and Bharathi, 2012). There are proofs for use of inhibitors since the early XIX century. During that time, inhibitors were used to protect metals in processes such as protection against aggressive water, acid pickling, acidified oil wells and cooling systems (Dariva and Galio, 2014). The use of inhibitors was really well known since 1950's and 1960's whereby now advanced technology was developed on inhibitors to prevent corrosion of metals.

Corrosion inhibitor is a compound which is added in a little amount and also small concentration in aggressive environment to prevent corrosion. Inhibitors have been commercialised in many fields such as cooling systems, refinery units, pipelines,

chemicals, oil and gas production units, boilers and water processing, paints, pigments, lubricants and a lot more (Raja and Sethuraman, 2008). For instance in oil industry, sodium carbonates or organic amines complex are employed to reduce the corrosive effect of CO₂, H₂S and organic acids, enabling the use of cheaper materials and less resistant to corrosion in wells extracting crude oil.

The mechanism of inhibitors is described as follows (Dariva and Galio, 2014):

- the inhibitor is chemically adsorbed (chemisorption) on the surface of the metal and forms a protective thin film with inhibitor effect or by combination between inhibitor ions and metallic surface;
- the inhibitor leads a formation of a film by oxide protection of the base metal;
- the inhibitor reacts with a potential corrosive component present in aqueous media and the product is a complex (Gentil, 2003, Ju et al., 2008).

Generally, corrosion inhibitors can be chemicals either synthetic or organic and they are classified by (Dariva and Galio, 2014):

- the chemical nature as organic or inorganic;
- the mechanism of action as anodic, cathodic or a anodic-cathodic mix and by adsorption
- action, or;
- as oxidants or not oxidants (Gentil, 2003).

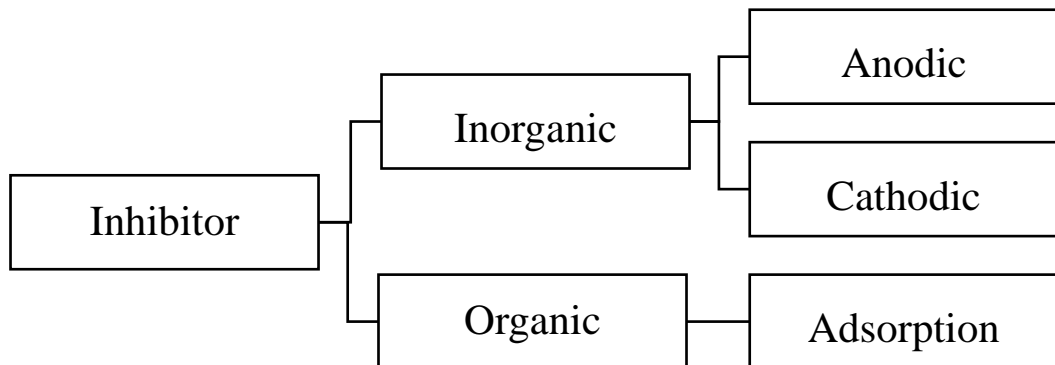


Figure 2.1: Classification of Inhibitors (Dariva and Galio, 2014)

i) Inorganic Inhibitors

a) Anodic Inhibitors

Anodic inhibitors also known as passivation inhibitors, act by blocking the anode reaction and supports the natural reaction of formation of light coat film which are adsorbed on the metal. Generally, the anodic inhibitors reacts with metallic ions Me^{n+} produced on the anode where it undergoes hydrolysis reaction, forming insoluble hydroxides (OH^-) ions. They are deposited on the metal surface and forming cohesive and insoluble which makes them impermeable to metallic ion (Gentil, 2003, Roberge, 1999). There are few examples for anodic inhibitors which are nitrates, molybdates, sodium chromates, phosphates, hydroxides and silicates. Figure 2.2 illustrates the mechanism of anodic inhibitors. For anodic inhibitors, the concentration needed to be high enough to ensure the metal is covered fully with the film.

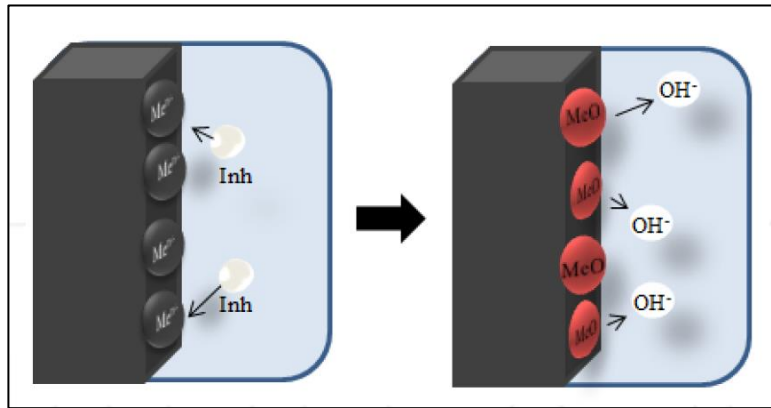


Figure 2.2: Illustration of anodic inorganic inhibitors effect and their mechanism of action (Dariva and Galio, 2014)

b) Cathodic Inhibitors

Cathodic inhibitors, either slows down the occurrence of the cathodic reaction of the metal during corrosion process or selectively precipitates insoluble compounds on cathodic sites. The mechanisms of cathodic inorganic inhibitors are depicted in the Figure 2.3 below:

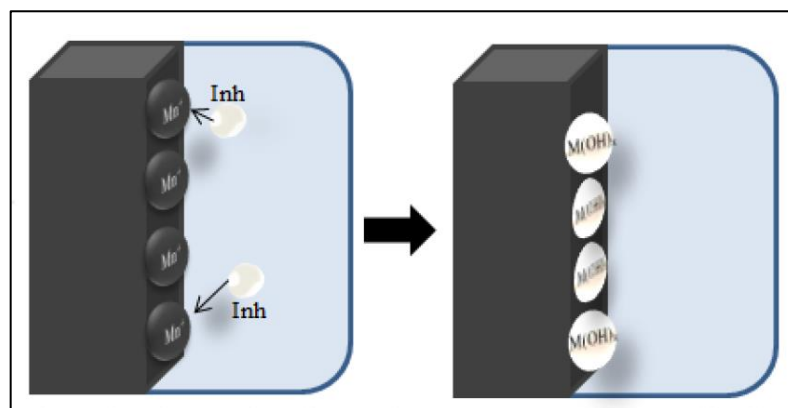


Figure 2.3: Mechanism of action of cathodic inhibitors (Dariva and Galio, 2014)

In general, these cathodic inhibitors produce cathodic reaction due to alkalinity with the presence of metal ions. As a result, insoluble compounds precipitate selectively forming

compact and adherent film on the metal surface. Thus, the film increase the resistivity of the metals and restrict diffusion of reducible species like oxygen and conductive electrons (Gentil, 2003, Roberge, 1999, Talbot and Talbot, 2000). Cathodic inhibitors are more secure than anodic inhibitors, since they are independent of the concentration. Examples of cathodic inhibitors are ions of the magnesium (Mg), zinc (Zn), and nickel (Ni) that react with the hydroxyl (OH^-) of the water forming the insoluble hydroxides which are $\text{Mg}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$ respectively.

i. Organic Inhibitors

Organic compounds used as inhibitors can act as either cathodic or anodic inhibitors, or else together, which is anodic and cathodic inhibitor. They also comply theory of surface adsorption, forming a protective hydrophobic film which acts as a barrier on the metal surface. Thus, the adsorbed film prevent the dissolution of metal. This organic inhibitors have low environmental risk and portrays good inhibition efficiency (Yaro et al., 2013), but they have to be soluble or dispersible in the medium surrounding the metal (Gentil, 2003). The Figure 2.4 shows the mechanism of organic inhibitors.

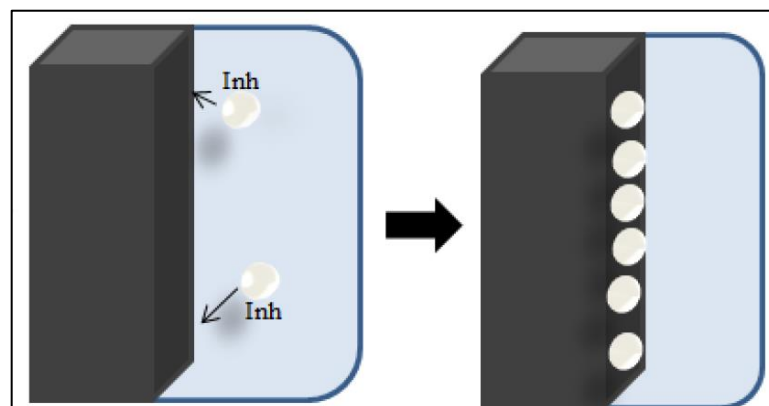


Figure 2.4: Mechanism of actuation of organic inhibitor
(Dariva and Galio, 2014)

Examples of organic inhibitors are mercaptobenzothiazole (MBT), aldehydes, succinic acid and lots more. Generally, these organic acid inhibitor that contains oxygen, nitrogen and/or sulphur is adsorbed on the metallic surface blocking the active corrosion sites. Though organic compounds have the π -bonds and claim to be the most effective and efficient organic inhibitors, they present biological toxicity and environmental harmful characteristics (El-Haddad, 2013).

2.5 Plant extract as a potential green corrosion inhibitor

Corrosion control of metals is of technical, economic, environmental, and aesthetical importance. The use of inhibitors is one of the best options of protecting metals and alloys against corrosion. Figure 2.5 below shows market demand of inhibitor for different fields in 2012.

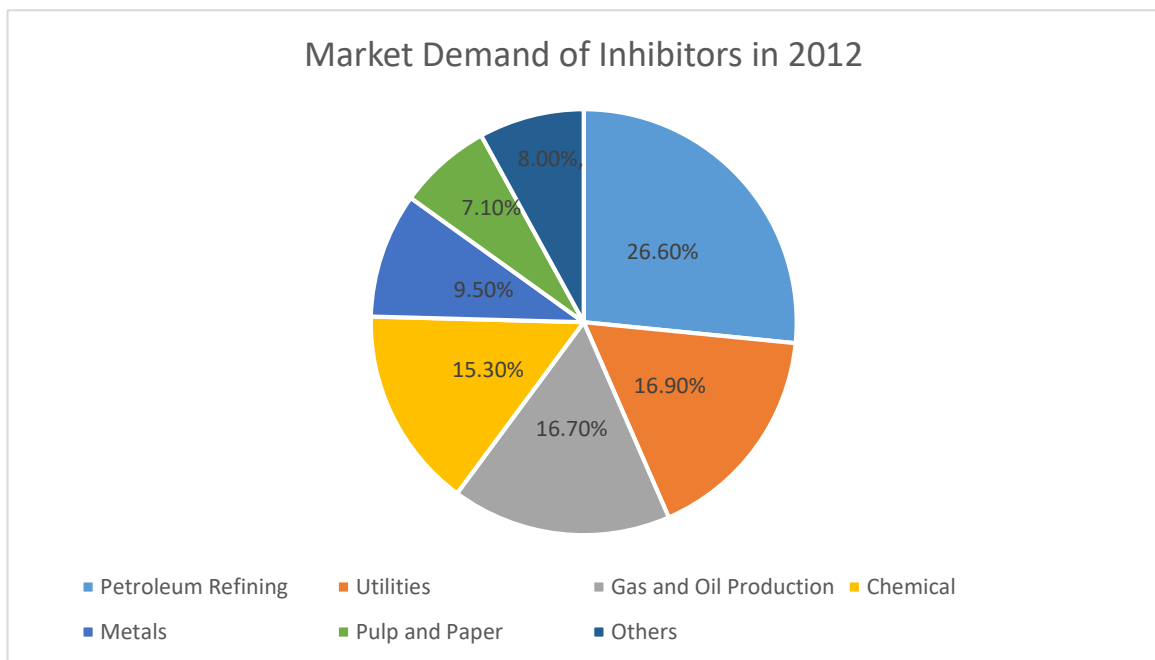


Figure 2.5: Market Demand of Inhibitors in 2012 (Dariva and Galio, 2014)

However, the presence of arsenic, chromate and other synthesized high toxic materials in corrosion inhibitor which cause health and environmental problems, strict laws were imposed to control their usage in industries (Dariva and Galio, 2014). These organic or inorganic inhibitors which contain synthesized materials are expensive and non-biodegradable. The environmental toxicity of synthetic corrosion inhibitors has prompted the search for green corrosion inhibitors as they are biodegradable, free from heavy metals or other toxic compounds.

Recently, there are several researches conducted which has explored the uses of natural products like plant extracts, essential oils and purified compounds as green corrosion inhibitors. This area of research is of much importance because natural products are inexpensive, readily available and renewable sources of materials, plant products are environmentally friendly and ecologically acceptable. Plant products are organic in nature and some of the constituents including tannins, alkaloids, saponins, essential oils, flavones, organic and amino acids are known to exhibit inhibiting action (Olabiyi et al., 2008, Chetouani et al., 2005, Umoren et al., 2008, Boukalah et al., 2006).

In addition to these organic materials, they contain polar functions and conjugated double bonds and aromatic rings, which are the major adsorption centers (Nnanna et al., 2014). Moreover, a research has stated that adsorption of natural corrosion inhibitors on metal surfaces is influenced by a number of factors including nature of metal, testing media, chemical structure of inhibitor, nature of substituents present in the inhibitor, presence of additives, solution temperature, and solution concentration (Verma and Quraishi, 2017). Examples of researches regarding green corrosion inhibitor:

Table 2.2: Green corrosion inhibitor used in researches for aluminium and its alloy in acid or alkaline solution

Green Corrosion Inhibitor	Metal/Alloy Protected	Medium (Acidic/Alkaline)	Inhibition Efficiency, η (%)	References
Azwain seed extract	Aluminium	0.5M HCl	90	Mary and Divya, (2017)
<i>Rauwolfia serpentina</i>	Aluminium	1M NaOH	97	Chaubey et al., (2017b)
<i>M. oleifera</i> tree bark extracts	Aluminium	1M NaOH	85.3	Chaubey et al., (2017a)
<i>M. oleifera</i> leaf extract	Aluminium	0.5M HCl	95	Nnanna and Owate, (2014)
<i>Prosopis cineraria</i>	Aluminium	0.1M HCl	96.93	Sharma et al., (2006)
<i>Capparis decidua</i> fruit extract	Aluminium	0.5M HCl	98.49	Mathur et al., (2007)
<i>Gossypium hirsutum L.</i> leaf extracts	Aluminium	2.0M NaOH	97	Abiola et al., (2009)

2.6 Method of Extraction for Natural Products

Phytochemically, extraction of bioactive compounds is defined as a separation procedure utilised for the recovery and purification of plant materials, proclaiming them

useful in a wide range of applications (Torres et al., 2017). There are numerous techniques involved for extraction of plant extracts. The conventional techniques like maceration and Soxhlet extraction are normally carried out to extract bioactive compounds like tannins, phenolics, flavonoids and so on. There are actually disadvantages in these conventional methods. One of them is high consumption of organic solvent limits the application of bioactive extracts due to its toxicity. Then, longer time of extraction is needed which also consumes higher energy as well as causing cost increment.

In order to replace these conventional techniques, novel extraction techniques with different mechanisms like Ultrasound, Microwave energy, Supercritical fluids and Accelerated solvent extraction has been implemented (Torres et al., 2017). Ultrasound assisted extraction stands out as a sustainable alternative compared to other techniques because:

- i. Moderate usage of solvent and energy
- ii. Easy to handle
- iii. Safe (Works at ambient temperature and atmospheric pressure)
- iv. Economical
- v. Reproducible

Ultrasonication works based on principle of acoustic cavitation which is capable of damaging the cell walls of the plant matrix and thereby favouring the release of bioactive compounds. This technology is suitable to obtain different phytochemicals of which phenolic compounds stand out. This technology is really useful in various fields of industry, particularly the food and pharmaceutical industries in which phenolic compounds have high importance and demand.

2.7 *Moringa oleifera* extract as a potential green corrosion inhibitor

M. oleifera, a *Moringaceae* family commonly known as drumstick or horseradish is rich in vegetable oil and high in nutritional values, is used in Asia as a vegetable and medicinal plant. *M. oleifera* has a diverse range of medicinal uses as an antioxidant, anticarcinogenic, anti-inflammatory, antispasmodic, diuretic, antiulcer, antibacterial, antifungal and its antinociceptive properties, as well as its wound healing ability has been demonstrated. Additionally, the root bark has been used as an analgesic, alexeteric, antihelminthic, and treatment for heart complaints, as well as for eye diseases, inflammation and dyspepsia. It is considered one of the world's most useful trees, as almost every part of the tree can be used for food, or has some other beneficial properties (Moyo et al., 2011). The leaves, especially young shoots, are eaten as greens, in salads, in vegetable curries, and as pickles. The leaves can be eaten fresh, cooked, or stored as dried powder for many months without refrigeration, and reportedly without loss of nutritional value. (Rodríguez-Pérez et al., 2015)

At the same time, research has been carried out to compare the anticorrosive nature of fruit extracts from different plants such as *M. oleifera* (*Moringaceae* family), *Piper longum* (*Piperaceae* family) and *Citrus aurantium* (*Rutaceae* family) on mild steel in 1M HCl. At 300 ppm concentration of each extract, the inhibition efficiency followed the order *M. oleifera* > *Piper longum* > *Citrus aurantium* (Sheeja and Subhashini, 2015). The result obtained has revealed that *M. oleifera* is a better and potential corrosion inhibitor compared to other plants. Other than that, leaf extracts of *M. oleifera* have also reported to exhibit antioxidant activity both in vitro and in vivo due to their abundance in phenolics and flavonoids.

2.8 Parameters Studied on Corrosion Inhibition of Aluminium

2.8.1 Effect of concentration of corrosion inhibitor

Concentration of inhibitor plays a major role in the inhibition efficiency. Many reported that higher concentration of inhibitor exhibits higher inhibition efficiency. For instance, Nnanna et al. (2014) reported that loss of weight of aluminium AA3003 reduced, as the concentration of the extract medium is increased. Therefore, it was concluded that corrosion rate of the metal decreased as the concentration of the inhibitor increases. This is mainly because the surface film of aluminium is amphoteric and dissolves when the metal is exposed to highly concentrated acids and bases. With the presence of inhibitor, there is a formation of compact adherent oxide film for its corrosion immunity which covers the aluminium surface. The thickness of this oxide film is dependent on the concentration of the inhibitor. Thus when the concentration increases, almost full coverage of the film causes the aluminium surface is less exposed and it eventually reduces the corrosion rate. For this experiment, the optimum concentration of inhibitor which exhibits maximum percentage of inhibition efficiency was 0.5 g/L.

2.8.2 Effect of temperature of corrosion inhibitor

When temperature of the corrosion inhibitors increases, the inhibitor efficiency was reported to reduce (Singh et al., 2016a, El-Etre, 2003, Aisha et al., 2017). As the temperature increases, there are chances for desorption of thin film from aluminium surface to occur. Therefore, dissolution of aluminium in the corrosive solution can take place which increases the corrosion rate.

2.8.3 Effect of period of immersion

Many researches have reported that the inhibition efficiency increases as the time of exposure becomes longer considering the inhibitor concentration. This is due to the formation of a protective film which grows with increasing exposure time. However, the efficiency of inhibitor only shows significant increase till it reaches the saturation level. As the immersion time increases, the physisorbed layer on the aluminium becomes thicker and this partially collapses (due to thickness) exposing the metal surface and hence inhibition efficiency decreases. Once the concentration of inhibitor has depleted, the immersion or exposure time give effect to the inhibition efficiency. Thus, it can be deduced that inhibition efficiency decreases as the immersion time increases (Müller, 2004, James et al., 2006, Umoren and Ebenso, 2008, Subramanyam et al., 1993).

2.9 Adsorption Isotherm and Kinetic Studies of *Moringa oleifera*

Adsorption of the organic molecules occurs as the interaction energy between molecule and metal surface is higher than that between the water molecule and the metal surface. Corrosion inhibition of metal is assumed to occur due to the adsorption of plant extracts onto the metal surface. If that is the situation, it is recommendable to investigate the possible adsorption mode by testing the experimental data obtained with several adsorption isotherms. By doing so, we can get a clear picture on mechanism of corrosion inhibition and also interaction of inhibitor and metal surface.

In general, adsorption isotherm study describes the adsorptive behaviour of organic inhibitors to know the adsorption mechanism (Hmamou et al., 2012). It depends mainly on the nature and charge of the metal surface, adsorption of solvent and other ionic species, electronic characteristics of the metal surface, temperature of the corrosion reaction and the electrochemical potential at solution interface (Adejoro et al., 2015).