EVALUATION OF *PANDANUS AMARYLLFOLIUS* LEAVES EXTRACT AS ECO-FRIENDLY CORROSION INHIBITOR OF MILD STEEL IN HYDRCHLORIC ACID SOLUTION

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BY

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Nur Allia binti Asri

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LIST OF SYMBOLS

	Symbol	Unit
C_r	Corrosion rate	mm/year
C_{inh}	Inhibitor concentration	g/L
E_a	Apparent activation energy	kJ/mol
IE	Inhibition efficiency	%
R	Gas constant	$\mathrm{J\ K^{-1}\ mol^{-1}}$
R^2	Correlation coefficient	-
T	Temperature	˚C
w_1	Weight loss of mild steel in uninhibited solution	g
w_2	Weight loss of mild steel in inhibited solution	g
ΔG	Apparent Gibbs free energy	kJ/mol
ΔH	Apparent enthalpy	kJ/mol
ΔS	Apparent entropy	kJ/mol
θ	Surface coverage	-
λ	Arrhenius constant	-

LIST OF ABBREVIATION

FTIR	Fourier transform infrared spectroscopy
GC-MS	Gas chromatogram mass spectrometry
HCl	Hydrochloric acid

PENILAIAN EKSTRAK DAUN *PANDANUS AMARYLLFOLIUS* SEBAGAI PERENCAT PENGKAKISAN KELULI LEMBUT YANG MESRA ALAM DALAM LARUTAN ASID HIDROKLORIK

ABSTRAK

Pengkakisan logam menjadi satu isu dalam industri mahupun aplikasi kehidupan seharian jika dilihat kesan kepada kehidupan dan keselamatan manusia, ekonomi dan alam sekitar. Kajian ini dijalankan untuk menilai potensi ekstrak daun *P. amaryllfolius* sebagai perencat kakisan kepada keluli lembut dalam asid hidroklorik. Dalam kajian ini, keupayaan merencat ekstrak daun *P. amaryllfolius* ke atas keluli lembut di dalam 1.0 M asid hidroklorik (HCl) dinilai pada kepekatan ekstrak yang berbeza (0.2-1.0 g/L) dan suhu medium asid hidroklorik yang berbeza (30-70 ˚C) dengan penambahan ekstrak daun. Keluli lembut direndam dalam medium yang tidak mengandungi perencat dan medium yang mengandungi perencat selama 24 jam dan purata pengkakisan dikira menggunakan kaedah kehilangan berat. Keupayaan ekstrak untuk merencat didapati meningkat naik seiring dengan kenaikan kepekatan dengan keupayaan optimum sebanyak 98.24% efisiensi pada kepekatan 0.6 g/L ekstrak dalam 1.0 M asid hidroklorik pada suhu sekeliling. Keupayaan ekstrak daun *P. amaryllfolius* untuk merencat didapati menurun dengan pertambahan suhu. Penjerapan garis sesuhu sebatian perencat pengkakisan kepada keluli lembut dikaji dan garis sesuhu yang dilukis menepati garis sesuhu Langmuir. Pemalar penjerapan, K_{ads} yang dikira dari garis sesuhu Langmuir ialah 0.1177 L/g menunjukkan penjerapan ekstrak *P. amaryllfolius* ke atas permukaan keluli lembut. Entalpi, ΔH dalam sistem yang tidak berperencat dan berperencat yang dikira masing-masing ialah 31.345kJ/mol dan 92.305 kJ/mol menunjukkan bahawa tindak balas endotermik telah berlaku. Entropi, ΔS yang dikira di dalam sistem tidak berperencat dan sistem berperencat masing-masing ialah 43.423 kJ/mol and -129 kJ/mol. Daripada parameter yang dikira, tenaga Gibbs, ΔG yang diperoleh daripada kajian ialah -11.81 kJ/mol dan menunjukan bahawa proses penjerapan fizikal mengambil bahagian untuk menghalang tindak balas pengkakisan daripada berlaku ke atas permukaan keluli lembut. Lapisan pelindung daripada sebatian perencat terbentuk di atas permukaan keluli lembut dikaji menggunakan mesin spektroskopi transformasian Fourier inframerah (FTIR) dan mesin kromatografi gas spektrometri jisim (GC-MS). Daripada analisis ini, didapati sebatian dengan kumpulan hidroksil yang bertanggungjawab bertindak sebagai perencat dalam ekstrak daun *P. amaryllfolius.*

EVALUATION OF *PANDANUS AMARYLLFOLIUS* LEAF EXTRACT AS ECO-FRIENDLY CORROSION INHIBITOR OF MILD STEEL IN HYDROCHLORIC ACID SOLUTION

ABSTRACT

Corrosion of metal has been a great deal in industry as well as life application concerning its impact on human life and safety, economics and environment. The study was done to evaluate the potential of *Pandanus amaryllfolius* extract as corrosion inhibitor for mild steel in hydrochloric acid (HCl) solution. In this study, the inhibition ability of *P.amaryllfolius* extract on mild steel in 1.0 M hydrochloric acid (HCl) was evaluated at different concentration of *P.amaryllfolius* extract (0.2-1.0 g/L) and temperature (30-70˚C) of acidic medium with addition of *P.amaryllfolius* extract. Mild steel coupon was immersed in uninhibited and inhibited HCl medium for 24 hours and corrosion rate was calculated using weight loss method. Inhibition ability of the *P.amaryllfolius* extract was found to increase with increasing concentration with optimum inhibition ability at concentration 0.6 g/L extract in 1.0 M of HCl with efficiency of 98.24% at ambient temperature. However, the inhibition ability of the extract was decreasing with increasing temperature. The adsorption isotherm of the inhibiting compound in the *P.amaryllfolius* extract on mild steel surface was studied and the isotherm plotted matches with Langmuir isotherm. The adsorption constant, K_{ads} calculated from Langmuir isotherm is 0.1177 L/g indicates the adsorption of *P.amaryllfolius* extract to the metal surface. Enthalpy, ΔH of uninhibited and inhibited system calculated are 31.345 kJ/mol and 92.305 kJ/mol, respectively shows that the reaction is endothermic. Entropy ΔS calculated for inhibited and uninhibited system are -43.423 kJ/mol and -124.91 kJ/mol respectively. From the parameters calculated, ΔG obtained from the studies is -11.81kJ/mol showing that physisorption process takes place to halt the corrosion reaction of mild steel. The protective film of inhibiting compound formed on mild steel surface was studied using Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography Mass Spectrometry (GC-MS). It was found from the results that the compound responsible for inhibiting ability of *P.amaryllfolius* extract are those with hydroxyl functional group.

CHAPTER ONE

INTRODUCTION

1.1 Corrosion of metals

Metals and alloys are highly demanded in industrial either for piping or instrumental construction purpose. However, metal and alloys especially mild steels are always subjected to metal degradation or known as corrosion as they are exposed to aggressive media (Sastri, 2011; Eddy et al., 2015). Metals reacts to stimulus of the external environment such as chemical, physical of mixed chemical and chemical which drives the degradation of the metals as reported by (Groysman, 2010). Corrosion happens when pure metals or alloys tend to react with corrosive medium forming a stable compound which will lead to metal deterioration (Roberge, 2008). Corrosion of metals and alloys have great impacts towards industries economic issues, safety of the industrial site and can also cause damage to environment (Revie and Uhlig, 2008; McCafferty, 2010).

There are several forms of corrosion based on apparent morphology of corrosion mentioned by Sastri, (2011) and Dongshan, (2014) which are general corrosion, local corrosion and pitting corrosion. Accident in Flixborough, England is one of the disasters in chemical plant caused by corrosion of stainless steel reactor which risks human life and safety (Crowl and Louvar, 2011). Hence, corrosion study is important in industry as well as in daily life application concerning human life and safety, cost of corrosion and material conservation (McCafferty, 2010).

Corrosion prevention can be done by several methods such as the use of corrosion inhibitor, surface treatment, coating and sealant, cathodic and anodic protection (Craig et al., 2006). The use of corrosion inhibitor is a common employed methods for corrosion control since its help to reduce and mitigate corrosion problems (Laamari et al., 2016). Corrosion inhibitor is a chemical substance which slowing down the corrosion rate of metals or mitigate the corroding effects of surrounding medium when added in a small concentration (Revie and Uhlig, 2008). Corrosion inhibitor can either be synthetic or natural. Corrosion inhibitor can be categorized by its chemical nature as organic or inorganic, the action mechanism either it is anodic or cathodic or both anodic-cathodic or by action of adsorption and as oxidants inhibitor or non-oxidants inhibitor (Dariva and Galio, 2012).

1.2 Problem statement

Corrosion is an event of deterioration of metal due to chemical attack or reaction with surrounding environment (Andreani et al., 2016). The practical way to control the corrosion of metal is by addition of corrosion inhibitors. Corrosion inhibitor can be in the form of liquid or vapor. Corrosion inhibitors mitigate corrosion of metals by altering the corrosive environment to non-corrosive environment or by interacting with the surface of metals and form a protection layer/barrier preventing metals from corrosion (Sastri, 2011).Organic or inorganic corrosion inhibitor contain heteroatom such as O, N, S, lone pair electron and π bond in their molecule are said to be effective in reducing the aggressiveness of metal corrosion (Farhat and Quraishi, 2011). Anyhow, the toxicity and biodegradability of inorganic corrosion inhibitors has prompted the studies of developing green inhibitors using plant extract as main source which are biodegradable and less toxic to environment when being discharged (Sastri, 2011).

P. amaryllfolius belongs to Pandanaceae family with palm-like trees or shrubs broadly distributed in moist tropical region (Salim et al., 2004). *P. amaryllfolius* plant is cultivated widely in Southeast Asia region such as Malaysia, Thailand, Indonesia as well as India. *P. amaryllfolius* leaves has been widely used in cooking as food colouring, flavouring and spices (Salim, Garson and Craik, 2004). *P.amaryllfolius* leaves extract has antihyperglycemic effect as reported by Chiabchalard and Nooron, (2015).

In this study, the inhibition ability of *P. amaryllfolius* leaves extract on mild steel in 1.0 M hydrochloric acid was evaluated using different concentration of *P. amaryllfolius* leaves extract and different temperature of hydrochloric acid using weight loss method. Thermodynamics and kinetics studies were carried out to evaluate the inhibition behaviour *P. amaryllfolius* extract on mild steel in HCl.

1.3 Research objective

The main objectives of this study are:

i. To identify the compound present in *P. amaryllifolius* leaves extract using gas chromatography-mass spectrometry (GCMS) and Fourier Transform Infrared Spectroscopy (FTIR) equipment

ii. To evaluate *P. amaryllifolius* leaves extract ability as corrosion inhibitor of mild steel in hydrochloric acid at different extract concentration and different temperature using weight loss method.

iii. To study the interaction between the inhibitor and metal surface, the adsorption mechanism and the adsorption isotherm of *P. amaryllfolius* leaves extract on the mild steel surface and thermodynamic characteristic involved in corrosion inhibition of mild steel coupon.

1.4 Scope of study

In this study, *P. amaryllfolius* extract was used as green corrosion inhibitor of mild steel in hydrochloric acid media. The plant extracts were prepared via drying of fresh *P.*

amaryllfolius leaves, grinding and sieving to allow a better contact of solvent with *P. amaryllfolius* powder. Solid-liquid extraction method was performed using Soxhlet extractor set using ethanol as extracting solvent. The extract was then dried using rotary evaporator. The effect of concentration of the leaves extract on corrosion inhibition with concentration ranging from 0.2 g/L to 1.0 g/L was observed, and optimum amount of concentration was chosen to be used in subsequent experiment. Next, effect of temperature of hydrochloric acid on corrosion inhibition with temperature ranging from 30˚C-70˚C was investigated. The inhibition efficiency and corrosion inhibition were calculated and graph to show the relationship were plotted.

CHAPTER TWO

LITERATURE REVIEW

2.1 Corrosion

The usage of metal in everyday life and industry gives an apparent insight of durability. However, all metals except for gold are chemically unstable in almost all environment in which the service of metal unfavourable and protective mechanism to ensure their serviceability in engineering and commercial applications (Talbot and Talbot, 1998). Corrosion is a progressive damage of a material due to reaction with environment and has become a major issue in industry (Andreani et al., 2016). Hence, corrosion study is important in industries because of economics, safety and conservation reasons (Revie and Uhlig, 2008; McCafferty, 2010).

Current research in corrosion are driven by the importance of economic factor in industries. In oilfield application, a large amount of total cost of oil and gas producing companies are represented by corrosion problem as it happens at all stages from downhole to surface equipment and processing facilities (Finšgar and Jackson, 2014). Operating problems and equipment maintenance are usually due to corrosion, causing recurrent partial and event total process shutdown, leading to severe economic losses.

Corrosion economics can be divided into direct costs and indirect costs. Direct costs are as capital costs, control costs and design costs (McCafferty, 2010). Capital cost involves cost of part replacement if the corrosion is severe and some parts of the equipment has been greatly damaged, hence a replacement is needed to avoid accidents. Control cost on the other hand, as reported by McCafferty, (2010) involving the cost of repairing, maintenance the good serviceability of the equipment as well as painting as a protective layer to prolong the durability of the equipment. While indirect losses are plant shutdown, product loss due to leakage of pipeline or unit operations and product contamination. This problems can be avoided if the application of corrosion prevention is practiced (McCafferty, 2010).

2.1.1 Corrosion mechanism

General corrosion is one of the common forms of corrosion (Sastri, 2011). General corrosion or usually known as uniform corrosion is an uniform distribution attack over an exposed metal surface as reported by Groysman, (2010). This phenomenon happens by a chemical or electrochemical reaction on the metal surface exposed to the corroding environment. Figure 2.1 shows the schematic diagram of a metal surface undergoes a general corrosion (Groysman, 2010).

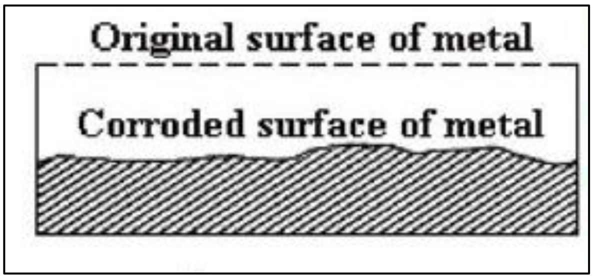

Figure 2.1: Schematic diagram of general corrosion forms

The thinning of metal surface in this corrosion mode may results in failure as loss of metal on tonnage basis is important. This form of corrosion can be mitigated by the use of corrosion inhibitor, proper choice of materials used or cathodic protection on the surface of the metal according to Sastri, (2011). Corrosion rate studies of this corrosion mode can be used to estimate the lifespan of the metals by evaluating the changes in the metal thickness, the weight loss of the corroding metal and measuring the volume of hydrogen gas evolves during the corrosion reaction when the metals are being immersed in the corrosive medium (Groysman, 2010).

Non-uniform or localized corrosion is more widespread than uniform corrosion due to the imperfections inside and outside of the surface of the metals and alloys (Groysman, 2010). Pitting and crevice corrosion are types of localized corrosion in metals as reported by Sastri, (2011). Localized morphologies are visualized in Figure 2.2.

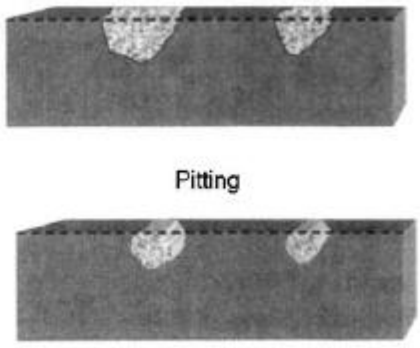

Figure.2.2(a): Pitting (Sastri, 2011)

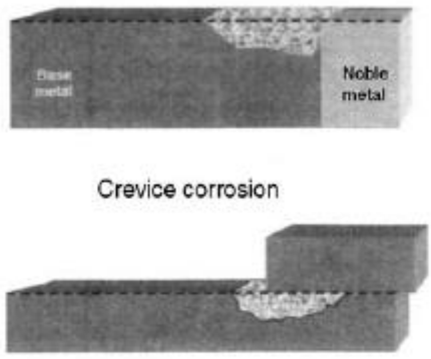

Figure 2.2(b): Crevice (Sastri, 2011)

Pitting initiates as a deep tiny hole pit and associated by the protective film breakdown on the metal surface (Schweitzer, 2007). Pitting is considered as unique anodic reaction and autocatalytic process (Sastri, 2011). Depth of pitting is expressed by the pitting factor, ratio of deepest metal penetration to average metal penetration which determined by the weight loss of metal specimen as mentioned in (Revie and Uhlig, 2008). The sketch of deepest pit relation with average penetration is illustrated in Figure 2.3

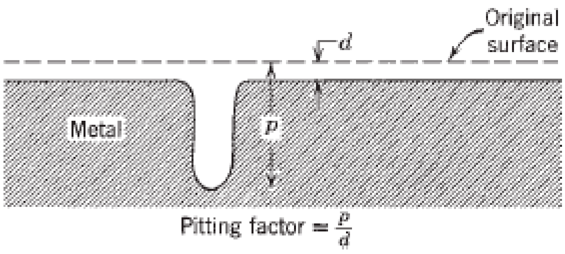

Figure 2.3:Sketch of deepest pit relation to average penetration (Revie and Uhlig, 2008)

As shown in Figure 2.2(b), crevice corrosion happened within or adjacent to narrow gaps or openings formed by metal-to-metal-to-non-metal contact as mentioned in

(Schweitzer, 2007). The gap is usually large enough to entrap liquid and become stagnant but too small to allow the flow of the liquid.

Corrosion is an electrochemical process and occurs through coupled electrochemical half-cell reactions of metals (McCafferty, 2010). As reported by Talbot and Talbot (1998), when two simultaneous reactions take place at interface between metal and an aqueous environment, it drives a corroding system. One is the reaction of which chemical species present in aqueous environment releases electron from the metal surface while the other reaction is the participation of metal surface atom to replenish the electron shortage. An electronic current is produced from electron exchange between the two reactions (Talbot and Talbot, 1998). The loss of metal occurs as an anodic reaction and the ideas is illustrated in Figure 2.4

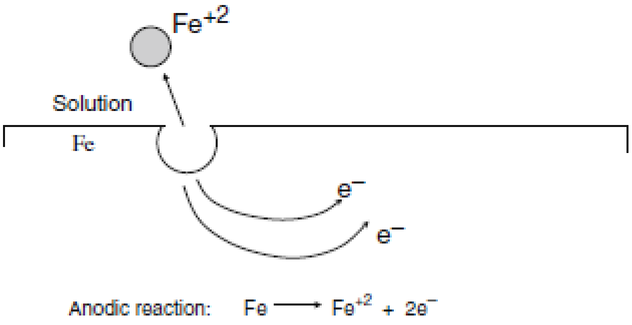

Figure 2.4(a): Anodic reaction- dissolution of iron (McCafferty, 2010)

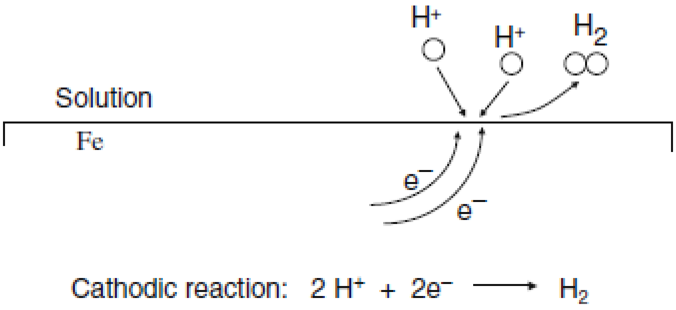

Figure 2.4(b): Cathodic reaction - hydrogen evolution

Figure 2.4(a) shows that iron has undergoes oxidation reaction where there is a loss of electron in anodic sites. On the other hand, a cathodic reaction is illustrated in Figure 2.4(b) shows that the hydrogen ions undergo reduction reaction producing 1 molecule of hydrogen gas. Hence, corrosion rate studies can be done by collecting the amount hydrogen gas evolved to determine the corrosion rate of a metals.

Two simultaneous reactions that drives the corroding system is known as coupled electrochemical reactions where anodic and cathodic reactions happens at different places on the metal surface simultaneously (McCafferty, 2010).

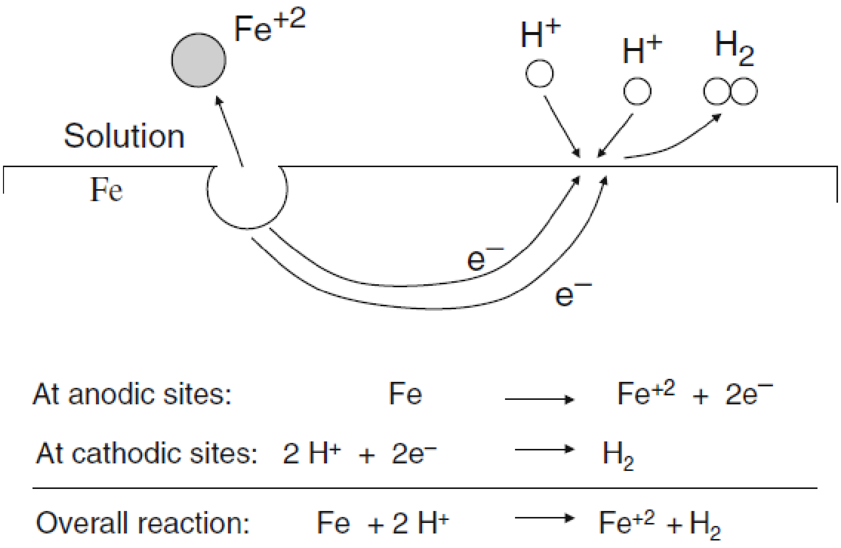

Figure 2.5: Visualization of coupled electrochemical reactions (McCafferty, 2010)

Figure 2.5 shows the four conditions for corrosion to occur which are an anodic reaction, a cathodic reaction, a metallic path of contact between anodic and cathodic sites and electrolyte presence (McCafferty, 2010). The reasons why two electrochemical half-cell reactions occur on the same metal is due to the heterogeneity of metal surface. The heterogeneity of metal surface can be illustrated in Figure 2.6.

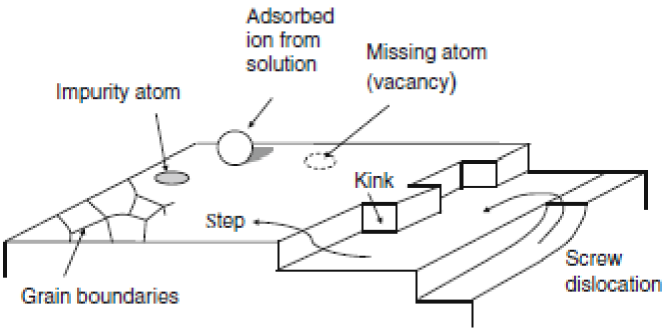

Figure 2.6: Heterogeneity of metal surface (McCafferty, 2010)

An array of site energies presence on polycrystalline metal surfaces due to grains and grains boundaries. Other defects such as edges, screw dislocations and point defects contributes to the heterogeneity of the metal surfaces (McCafferty, 2010).

2.2 Methods of preventing corrosion

There are several methods to prevent corrosion, and several researches has been done to studies the effectiveness of the prevention methods.

2.2.1 Surface Treatment

Surface treatment purpose is to increase the energy level of particular metals surface so that it can easily adhere to the coating of the metal surface. Surface treatment also known as coating pre-treatment creates a barrier acting as a protecting wall on the metal surface in a corrosive environment (McCafferty, 2010). Nitriding is one of the surface treatment processes which involves in process of exposing ferrous metal to heated ammonia derived conditions with active nitrogen presence forming a surface rich of nitrogen layer with complex nitrides (Girell et al., 1985; Bottoli et al., 2018). As reported by Girell et al. (1985), surface treatment by nitriding process showed an improvement in pitting resistance, where no pitting was found after low temperature nitriding process.

Other than that, a study conducted by Zhang et al. (2018) reported that application of low-temperature liquid nitriding on stainless steel shows high corrosion potential of Ecorr= -0.277V and low corrosion current density Icorr = 0.010A/cm2. This proves that nitriding surface treatment provides a superior corrosion resistance of stainless steel by forming a good barrier halting localized attack on metal surface.

2.2.2 Surface coating

Surface coating is a continuation of surface treatment of metals. After pre-coating pre-treatment or surface treatment of the metals, coating is applied to halt the corrosion attack on metal surface by a protective layer formed by the coating. Zinc electrodeposition on steel materials to prolong the serviceability has been notably used in industrial applications as reported by Atuanya et al. (2018). According to Bai et al. (2018), stainless steel coated with alumina forming β-NiAl coating by high velocity oxy-fuel (HVOF) spraying technique is well protected for 250 h exposure to corrosive medium. However, severe corrosion can be observed after 250 h due to fast growth rate of Al_2O_3 as chloride ions and O_2 started to diffuse and corroding the steel surfaces. However, another study conducted by Atuanya et al. (2018) reported that 99.02% corrosion resistance can be achieved by steel coated by Ni-Co-25SiO_2 due to hard and fine structure obtained by the metal surface after coating. Morphological studies also show that Ni-CO-25SiO_2 average particle size is small which prevent corrosive medium from attacking the steel surface.

2.3 Corrosion inhibitor

It is nearly impossible to halt corrosion in industries, but possibility of controlling the corrosion rate is achievable (Finšgar and Jackson, 2014). Corrosion prevention using corrosion inhibitor is one of the known methods of corrosion control among various method to halt the destruction of metal surface. In acidic media, the compound responsible in inhibiting corrosion reported are nitrogen-base materials and their derivatives, sulphur-containing compounds, aldehydes, thioaldehydes, and various alkaloids (Sastri, 2011). Inhibitors are chemical reacting with the material surface to decrease the rate of corrosion or interacting with the operating medium to reduce the corrosivity of the medium (Craig et al., 2006).

Inhibitors reduces or controls the reaction of metal with surrounding media thus, reducing the corrosion rate by ions or molecules adsorption on the metal surface, increasing or decreasing of anodic or cathodic reaction and decreasing the diffusion rate of reactants to the metal surface (Craig et al., 2006; Dariva and Galio, 2012). The mechanism of the inhibitor can be described by chemisorption of inhibitor on the metals surface forming a thin film barrier protecting the metal surface from corrosion. Corrosion can be classified into certain types, Figure 2.7 shows the classification of inhibitor.

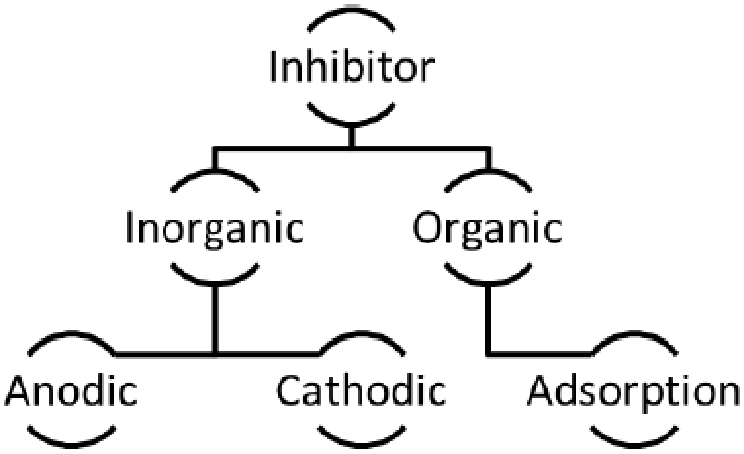

Figure 2.7: Classification of corrosion inhibitor

2.3.1Anodic inhibitor

Anodic inhibitor is also known as passivation inhibitor. It acts by reducing anodic side, by blocking anode reaction and forms a film adsorbed on metal surface which supports the natural reaction of metal surface passivation. Passivating inhibitors cause an anodic shifting to force the metallic surface into passivation range (Schweitzer, 2010). By other means, inhibitor is actually reacts with metal surface thus forming a compact barrier to prevent further metal degradation (Craig, et al., 2006; Dariva and Galio, 2012). Metallic ions Me^{n+} produced on the anode is reacting with anodic inhibitors, thus, and insoluble film formed from insoluble hydroxides deposited in the metal surfaces. Passivation inhibitor can be either oxidizing such as nitrites, nitrates and widely used chromates or non-oxidizing such as phosphate and molybdates (Craig et al., 2006; Roberge, 2008). Oxidizing inhibitors does not require oxygen to be present in the environment whereas oxygen must be present in environment containing non oxidizing inhibitor (Craig et al., 2006). As mentioned in Schweitzer (2010), concentration of anodic inhibitor must be above certain critical values or else, the corrosion rate in localized area might increase due to behaviour of anodic inhibitors as active depolarizers below critical concentration. Lower concentration of inhibitors attribute to active value of oxidation-reduction potential and causing the intersection of cathodic polarization curve with anodic curve in active region instead of in passive region.

2.3.2 Cathodic inhibitor

Cathodic reaction of metals is prevented by cathodic inhibitor during corrosion process. Cathodic inhibitor inhibit the hydrogen gas formation in acidic medium or oxygen reduction in neutral or alkaline solution (Sastri, 2011). Metal ions present in this inhibitor makes the inhibitor able to produce cathodic reaction due to alkalinity, forming insoluble compounds that precipitates of cathode sites. The impedance of the surface is increasing (Dariva and Galio, 2012). Calcium bicarbonates, zinc compound and polyphosphate are examples of cathodic inhibitor (Craig, et al., 2006).

A study conducted by Hamdy (2006) shows that surface treatment with cerium sol gel coating does enhance the localized corrosion of aluminium in NaCl for 30 days with surface resistance of 7.4×10^4 ohms and the inhibitors acts as an cathodic inhibitor on aluminium.

2.3.3 Green corrosion inhibitor

Researchers' attentions have shifted towards the applications of green corrosion inhibitors associated with the awareness of protecting the environment (Cang et al., 2013). The shifting of inorganic inhibitor to green corrosion inhibitor are due to its biodegradability and non-toxicity as there are no heavy metals and toxic compound present in the inhibitor (Sastri, 2011).

Besides, good inhibition ability of plant extract on metals has been seen in previous researches. Corrosion inhibition of mild steel in sodium chloride solution using the extracts of *Ricinus communis* leaves reported by Sathiyanathan et al., (2005) shows a good ability of reducing the corrosion rate with 85% of inhibition efficiency at 300 ppm concentration of extracts. Other than that, Yaro et al. (2013) studies reported that apricot juice has the ability to inhibit corrosion of mild steel with maximum inhibition efficiency of 75% at 30˚C and maximum level of inhibitor concentration in acidic medium. Adsorption of inhibitor in apricot juice studied by Yaro et al. (2013) satisfies Langmuir adsorption isotherm with monolayer formation on metal surface and the results were verified by thermodynamic studies of adsorption model. Similar observation was shown in aluminium corrosion study conducted by Singh et al. (2016) with corrosion inhibition efficiency of 94% with inhibitor concentration of 400 mg/L in NaOH medium. It can be seen that most of green corrosion inhibitor forms a protective film or barrier to halt the attack of corrosive medium on metal surface.

Corrosion inhibition is associated with the phytochemical compound present in the plant extract (Okafor and Ebenso, 2007). The effectiveness of plant extract in inhibiting the corrosion rate of metals is attributed to the presence of suitable functional group such as lone pair electron rich functional system, presence of hetero atoms in the bioactive compound, presence of conjugated system and possession of aromatic ring or long carbon chain with presence of hetero atom in it (Sastri, 2011; Muthukrishnan et al., 2015). Recent studies of plant extract as green corrosion inhibitor source are summarized as Table 2.1:

Table 2.1: List of green corrosion inhibitors

Metal	Inhibitor source	Medium	Active Ingredient	IE%	Reference
Mild steel	Aloe leaves	HCl	Aloeemodin, Aloin-Barbaloin	71.66	(Cang *et al.*, 2013)
Mild steel	*Zenthoxylum alatum*	HCl	Isooxazolidine, imidazolinedione	95.00	(Chauhan and Gunasekaran, 2007)
Mild steel	*Myrmecodia pendans*	HCl	6-benzylaminopurine	73.33	(Pradityana *et al.*, 2017)
Mild steel	*Punica granatum* (pomegranate)	HCl	Gallic acid, granatin-B	99.00	(Ashassi-Sorkhabi *et al.*, 2015)
Mild Steel	*Carica papaya*	H_2SO_4	Anthraquinones, saponins and tannins	85.80	(Okafor and Ebenso, 2007)
Carbon steel	Garlic	HCl	Allyl methyl disulphide	97.00	(Pereira *et al.*, 2012)
Mild Steel	*Canna Indica* flower	HCl	Glycoside, Tannin, Terpene	91.48	(Mathina and Rajalakshmi, 2016)
Aluminium	*Ipomoea invulcrata*	HCl	d-lysergic acid amide (LSA)	89.10	(Obot *et al.*, 2010)
Aluminium	*Laurus nobilis* L. oil	NaCl	1,8-cineole, cyclic ethers, terpenoids	90.20	(Halambek, Berković and Vorkapić-Furač, 2013)
Aluminium	*Ficus tricopoda* gum	H_2SO_4	Sucrose, 2-methylene-3-ol, camphene 7-hexadecenal	85.80	(Eddy *et al.*, 2013)

2.4 *Pandanus amaryllfolius* leaves extract as a potential green corrosion inhibitor

Corrosion study has been very important recently as degradation of metals has caused lots of problems not only to industry sector but in daily life application as well. *P.amaryllfolius* has the potential as green corrosion inhibitor as recent studies has proved that *P amaryllfolius* leaf extract contains tocopherols, tocotrienols, alkaloid fatty acids, carotinoids and flavonoids which act as natural antioxidants compound and antidiabetic agents (Chiabchalard and Nooron, 2015). The compound present in *P. amryllfolius* has promising ability as corrosion inhibitor (Salim et al., 2004)

2.5 Parameters studied in corrosion inhibition of plant extract

Various parameters have been studied in corrosion inhibition using plant extract. Concentration, temperature and exposure time are the most common parameters being studied.

2.5.1 Effect of inhibitor concentration

Inhibition efficiency of plant extract on metal surface increases with increasing concentration of plant extract. This can be seen in a study conducted by Vimala et al., (2011) where the inhibition efficiency was the highest at inhibitor concentration of 0.15% v/v. Other than that, Murthy and Vijayaragavan (2014) reported that, the inhibition efficiency increased with the increasing concentration of *Hibiscus sabdariffa* leaves extract. Increase in inhibition efficiency may be because of increasing number of molecules occupied by the inhibitor. However, further increase in extract concentration after the maximum inhibition efficiency showed drops in efficiency because the compound in plant extract might undergone desorption process from the metal surface due to increase in ferrous ion concentration as reported by Vimala et al., (2011).

2.5.2 Effect of temperature

On the effect of temperature, factor Cang et al. (2013) reported that corrosion rate increases with increasing temperature but there is decrease in corrosion inhibition efficiency. The best inhibition efficiency reported by Cang et al. (2013) was at temperature of 30˚C. This suggests that at high temperature, the adsorption strength of plant extract to metal surface decreases implying physisorption process (Al-Otaibi et al., 2013).

2.6 Mild steel corrosion in acidic solution

Mild steel is a low carbon steel with carbon as its major constituents which widely used in industrial application for the process involving acid, alkali and salt solution (Sastry and Rao, 1981). Mild steel is neither brittle nor ductile, hence used in large quantities as structural element as it is cheap and ductile makes it a versatile alloy to be used in various application (Othman Ahmed et al., 2018). However, mild steel has low resistance towards corrosion especially in acidic environment (Alaneme, et al., 2016). The surface of mild steel may have mill scale or corrosion products due to destructive attack chemically or electrochemically. Mild steel corrosion in acidic medium is one of the most usual forms of corrosion (Shukla and Ebenso, 2011).

Acid and mild steel are widely used in several industrial process such as acid cleaning and etching, where the removal of rust and scale on metal surface are being done using acid as reported by Mathina and Rajalakshmi, (2016). Metal surface is often exposed and in contact with acid solution during this process, which eventually makes the reaction between metal surface and the corrosive medium active. To avoid gradual damage of the metal surface, several corrosion controls have been done, and the use of corrosion inhibitors is one of the best options to halt metal corrosion.

2.7 Adsorption isotherm and kinetic studies of corrosion inhibition

Surface coverage data is important to show the performance of organic adsorbent-type inhibitor, adsorption isotherms are usually used to explain the mechanism of inhibition as they relates the concentration of the inhibitor in solution to the amount of inhibitor present on the metal surface (Leelavathi and Rajalakshmi, 2013). The degree of surface coverage, θ was used to evaluate the best isotherm that fits the data.

There are several types of adsorption isotherms frequently used to describe the adsorption process are Langmuir, Temkin, Frumkin and Flory-Huggins, but Langmuir and Temkin isotherm are the most important isotherms belong to corrosion inhibition (McCafferty, 2010). The type of adsorption isotherm can give extra information regarding the properties of the test compound in plant extract and the adsorption depends on the compound chemical composition, the temperature and the electrochemical potential at the metal/solution interface (Cang *et al.*, 2013). According to Langmuir adsorption isotherm, θ is connected to equilibrium adsorption constant (K_{ads}) and C_{inh} by Equation 2.1;

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{2.1}$$

Where,

C_{inh} is concentration of inhibitor

K_{ads} is adsorption constant

θ is fraction if surface covered by the concentration of inhibitor

2.8 Thermodynamic aspect takes place in corrosion inhibition

To understand inhibitive mechanism of corrosion process, temperature plays a major role in the process. Arrhenius equation is used to express the relationship between corrosion rate of mild steel in acidic media and temperature (Shukla and Ebenso, 2011)

$$\log(C_r) = \frac{-E_a}{2.303\ RT} + log\lambda \qquad (2.2)$$

Where,

E_a is the apparent effective energy,

R is molar gas constant

λ is the Arrhenius pre-exponential factor

A plot of log of corrosion rate obtained by weight loss measurement vs 1/T produce a straight line. Shukla and Ebenso, (2011) reported that increase in apparent activation energy will results in significant decrease in adsorption of inhibitor on mild steel surface.

The behaviour of adsorption process can be determined from thermodynamics studies by calculating the hermodynamics parameter such as free Gibbs energy ΔG, apparent entropy activation ΔS, apparent enthalpy of activation ΔH, can be obtained from the alternative plot of $\log\left(\frac{C_r}{T}\right)$ against 1/T as reported by Cang et al. (2013).

CHAPTER THREE

MATERIALS AND METHOD

3.1 Materials and Chemical

In this study, *P. amaryllfolius* leaves was extracted with ethanol using Soxhlet extraction method. The list of chemicals used in this experiment were summarized in Table 3.1

Table 3.1:List of chemicals used in corrosion inhibiton experiment

Material & Chemicals	Purity	Supplier
Ethanol	95%	Fisher-Scientific Chemicals
Methanol	HPLC grade	Fisher-Scientific Chemicals
Hydrochloric acid	37%	Fisher-Scientific Chemicals
Dimethyl sulfoxide (DMSO)	-	Sigma Aldrich

3.2 Equipment

The extraction of *P. amaryllfolius* leaves were done using Soxhlet extractor set. *P. amaryllfolius* leaves were dried before extraction can be done. There are several equipment required for conducting the experiment. The list of equipment and their purposes were summarized in Table 3.2

Table 3.2: List of equipment used in corrosion inhibition experiment

Equipment	Purpose
Oven	To dry fresh *P. amaryllfolius* leaves
Grinder	To grind dried *P. amaryllfolius* leaves into smaller particle size
Sieve Shaker	To sieve ground *P. amaryllfolius* powder into particle size range of 250-500 micrometres
Heating Mantle	To heat up ethanol to vaporize

Table 3.2: Continued

Soxhlet Extractor set	To extract the bioactive compound in *P. amryllfolius* leaves
Rotary Evaporator	To dry *P. amaryllfolius* leaves extract
Water Bath Shaker	To heat up hydrochloric acid to desired temperature during the effect of temperature study
GC-MS	To identify the bioactive compound present in *P. amaryllfolius* leaves extract
FTIR	To characterize *P. amaryllfolius* leaves extract

3.3 Experimental Activities

Experimental activities were planned to ensure that the experiment was done smoothly. The experimental activities were summarized as shown in Figure 3.1

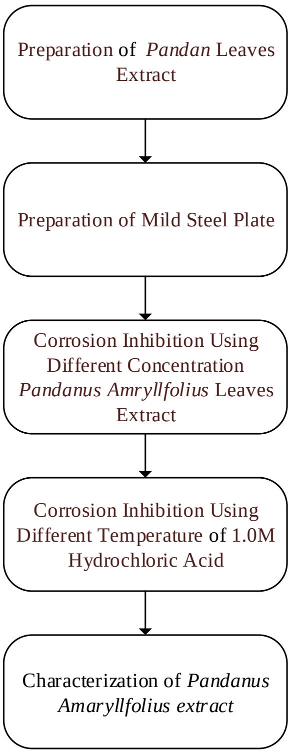

Figure 3.1: Schematic flow diagram of experimental activities

3.4 Experimental procedure

3.4.1 Preparation of *Pandanus amaryllfolius* leaves extract

Fresh *P.amaryllfolius* leaves were dried using oven at temperature of 50˚C for 24 hours. Dried *P.amaryllfolius* leaves were then grinded into powder from with particle size ranging from 250-500 micrometres. Extraction of *P.amaryllfolius* leaves was performed using Soxhlet extraction method for 7 hours using 95% ethanol as extractive solvent with heating mantle temperature set to 120˚C (Bimakr *et al.*, 2011; Verran *et al.*, 2014). Thimble containing 7g of *P.amaryllfolius* leaves powder was wetted by the dripping of ethanol condensate in the extractor. Ethanol containing *P.amaryllfolius* extract filled up the siphon arm and recirculated. The mixture of ethanol and *P.amaryllfolius* extract were dried using rotary evaporator at temperature of 80˚C until all the ethanol dried. The dried extract was then scrapped off and kept in refrigerator at temperature of 4˚C.

3.4.2 Preparation of mild steel plate

Mild steel with dimension of 3 cm x 5 cm x 0.1 cm was polished using sandpaper and degreased with acetone and washed with distilled water. Mild steel plates were then dried and kept in dessicator until further use.

3.4.3 FTIR and GCMS analyses

GCMS equipment is used to identify the compound present in *P.amaryllfolius* leaves extract. Concentrated *P.amaryllfolius* leaves extract were diluted in methanol HPLC grade. The diluted extract was then filtered and filled in a sample bottle before being sent for GC-MS testing.

To identify the corrosion inhibitory compound present, FTIR spectrometer is used. The surface of mild steel was being scrapped off using emery paper after being immersed in HCl solution containing *P. amaryllfolius* leaves extract to obtain the surface powder. The powder was then scanned within wavelength ranging from 500-4000 $\text{cm}^{-1}$and potassium bromide (KBr) pellet was used as a support in the analysis.

3.4.4 Corrosion Inhibition Studies

The initial weight of mild steel before being immersed in 1.0 M hydrochloric acid and final weight of mild steel after 24 hours immersion was recorded and the difference in weight was calculated using mass balance. The average difference in weight is calculated and a graph was plotted to show the relation of corrosion inhibition with concentration and temperature. Percentage of corrosion inhibition efficiency was calculated using equation (3.1)

$$IE\% = \frac{w_1 - w_2}{w_1} \times 100\% \tag{3.1}$$

Where,

w_1 and w_2 is the weight loss of mild steel in uninhibited and inhibited solutions (Pereira *et al.*, 2012)

IE% is the corrosion inhibition efficiency percentage

3.4.5 Corrosion inhibition in different concentration of *Pamdanus amaryllfolius* leaves extract

P. amaryllfolius leaves extract were diluted to concentration of 0.2 g/L, 0.4 g/L, 0.6 g/L, 0.8 g/L and 1.0 g/L in separate beakers containing HCl with a volume of 80 mL. A control was prepared in a beaker containing only 80 mL of 1.0 M hydrochloric acid. Mild steel coupons initial weight used was weighed using digital