Trigona sp. AND Apis sp. HONEY AS NATURAL CORROSION INHIBITOR FOR ALUMINIUM ALLOY IN 1 M PHOSPHORIC ACID

by

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CPE	Constant phase element
CR	Corrosion rate
EIS	Electrochemical Impedance Spectroscopy
EDX	Energy Dispersive X-Ray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
H_3PO_4	Phosphoric acid solution
IE	Inhibition Efficiency
Mpy	Mils of penetration per year
PZC	Potential Zero Charge
SEM	Scanning Electron Microscopy
XRF	X-Ray Fluorescene Spectroscopy
E_a	Activation energy
E_{corr}	Corrosion potential
E_{pit}	Pitting potential
E_r	Antropy ‘rational’ corrosion potential
E_{rp}	Repassivation potential
i_{corr}	Corrosion current density
ΔH	Enthalpy change (kJ mol^{-1})
ΔS	Entropy change (J K^{-1} mol^{-1})
ΔG_{ads}	Gibbs free energy change (kJ mol^{-1})
mA cm^{-2}	Miliampere per centimetre square

mm y^{-1}	Milimetres per year
mV	Milivolt
mV s^{-1}	Milivolt per second
R_{ct}	Resistance charge transfer
R_p	Polarization resistance
R_s	Solution resistance
R^2	Regression coefficient
v/v	Volume per volume
w/v	Weight per volume
Ω cm^2	Ohm’s centimetre square

MADU *Trigona* sp. DAN *Apis* sp. SEBAGAI PERENCAT KAKISAN SEMULA JADI BAGI ALOI ALUMINIUM DALAM 1 M ASID FOSFORIK

ABSTRAK

Dua jenis sampel madu, madu kelulut (*Trigona* sp.) dan madu lebah (*Apis* sp.) telah dipilih dan dikaji sebagai perencat kakisan bagi aloi aluminium dalam larutan 1 M asid fosforik (H_3PO_4). Kajian pencirian telah dijalankan untuk menentukan kumpulan fungsi dalam madu yang bertanggungjawab dalam proses perencatan. Keputusan spektroskopi inframerah Fourier transformasi (FTIR) menunjukkkan kewujudan kumpulan fungsi utama yang boleh memenuhi ciri keperluan sebagai perencat kakisan organik yang baik. Analisis kedua-dua madu dengan menggunakan spektroskopi jisim kromatografi cecair dengan menggunakan kolum C18 fasa berbalik menunjukkan kehadiran asid p-kumarik di dalam madu yang merupakan salah satu daripada sebatian fenolik yang mempunyai kapasiti antioksida tertinggi. Kandungan fenolik dan kapasiti antioksida madu kelulut didapati lebih tinggi daripada madu lebah. Peratusan keberkesanan perencatan (IE %) kedua-dua madu telah disiasat dalam 1 M H_3PO_4 menggunakan kaedah penentuan kehilangan berat, pengukuran potensiodinamik, dan pengukuran spektroskopi impedans elektrokimia (EIS). Kajian mendapati bahawa IE % kedua-dua madu tersebut bertambah dengan pertambahan kepekatan madu yang digunakan. Berdasarkan pengukuran kekutuban potensiodinamik, nilai IE % paling tinggi didapati pada kepekatan optima (1500 ppm) iaitu 78.6 % bagi madu kelulut dan 73.9 % bagi madu lebah. Pengukuran kekutuban potensiodinamik menunjukkan bahawa kedua-dua madu bertindak sebagai perencat jenis campuran dengan kesan perencat anodik lebih dominan. Pengukuran EIS telah menunjukkan bahawa kakisan aloi aluminium dengan kehadiran atau ketidak hadiran perencat adalah secara amnya dikawal oleh proses permindahan cas. Kakisan liang telah disiasat dengan menggunakan pengukuran kekutuban berkitar yang mendapati bahawa luas gelung histeresis bagi larutan 1 M H_3PO_4 tanpa madu adalah lebih besar berbanding larutan yang mengandungi madu. Keputusan ini menunjukkan bahawa keamatan kakisan liang aloi aluminium adalah lebih kecil dalam larutan 1 M H_3PO_4 dengan kehadiran madu berbanding dengan ketiadaan madu. Penentuan kehilangan berat pada suhu yang berbeza menunjukkan bahawa IE % bagi madu kelulut dan madu lebah semakin berkurang dengan peningkatan suhu. Kajian isoterma penjerapan menunjukkan bahawa perencat mengikuti model penjerapan Langmuir. Keupayaan cas sifar (PZC) menunjukkan madu kelulut dan madu lebah terjerap ke permukaan aloi aluminium secara fizikal. Analisis permukaan dengan mikroskop elektron imbasan menunjukkan permukaan aloi aluminium yang lebih baik atau kurang mengalami kakisan dengan kehadiran perencat madu kelulut.

***Trigona* sp. AND *Apis* sp. HONEY AS NATURAL CORROSION INHIBITOR FOR ALUMINIUM ALLOY IN 1 M PHOSPHORIC ACID**

ABSTRACT

Two types of honey samples, stingless bee honey (*Trigona* sp.) and natural honey (*Apis* sp.) were selected and studied as aluminium alloy corrosion inhibitor in 1 M phosphoric acid (H_3PO_4). The characterization studies have been conducted to determine the heteroatoms in honey that are responsible for inhibition process. Fourier transform infrared (FTIR) spectroscopy results suggest the presence of important functional groups that fulfilled the requirement as a potent organic corrosion inhibitor. The analysis of both honeys by liquid chromatography mass spectrometry with a reversed phase C18 column was done and the analysis showed evidence on the presence of p-coumaric acid, one of the phenolic compounds that has the highest antioxidant capacity. The phenolic content and antioxidant capacity showed stingless bee honey have the highest content compared to natural honey. The percentage inhibition efficiency (IE %) of the honeys were investigated in 1 M H_3PO_4 by means of weight loss method, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurement. These analysis showed IE % for both honeys increased with the increasing of the concentration of honeys. Potentiodynamic polarization method gave the highest IE %, which were 78.6 % for stingless bee honey and 73.9 % for natural honey at optimum concentration (1500 ppm). Potentiodynamic polarization measurement indicated that the inhibitors act as mixed type inhibitors with predominant anodic inhibition. EIS measurement showed that the corrosion of aluminium alloy with and without inhibitors was mainly controlled by a charge transfer process. Pitting corrosion was investigated by using cyclic polarization, which revealed that the area of the hysteresis loop of the 1 M H_3PO_4 solution without inhibitors was larger than that of the inhibitors. Thus, it indicated that the intensity of pitting corrosion was smaller in the 1 M H_3PO_4 with honeys when compared to the aluminium alloy without honeys. Weight loss measurements at different temperatures showed that the inhibition efficiencies for stingless bee honey and natural honey decreased as the temperature increased. The adsorption isotherm study revealed that the inhibitor follows Langmuir adsorption model. Based on the potential zero charges (PZC) it indicated that the adsorption on the aluminium alloy surface was by physical adsorption. The scanning electron micrographs showed that the surface of the aluminium alloy had improvement in the presence of the stingless bee honey.

CHAPTER ONE

INTRODUCTION

1.1 Background of study

Corrosion studies of aluminium and its alloys have received considerable attention because of their technological importance and industrial application. Aluminium and aluminium alloys are mainly used as parts in automobiles, aerospace and building structures, household appliances, containers and electronic devices (Philip and Schweitzer, 2003; Vargel, 2004). A remarkable economic and industrial importance of aluminium and its alloy are due to their low cost, light weight, high thermal and electrical conductivity. Additionally, aluminium and its alloy have good corrosion resistance toward the atmosphere and many aqueous media due to the formation of thin and highly protective oxide film which protects them from further corrosion. However, in the presence of aggressive environments the protective layer can be destroyed and corrosive attack takes place (Abd El Rehim *et al.*, 2004; Elewady *et al.*, 2008).

Acid pickling is one of the industrial cleaning processes used for removal of scales or oxide on the metallic substrates. The main acids abundantly used in industries are hydrochloric and sulphuric acid. One of the severe problems, in using these acids, is corrosion of metallic substrates. Phosphoric acid medium is widely used for acid cleaning and electro-polishing of aluminium and its alloys (Kuo and Tsai, 2000; Vargel, 2004; Ghulamullah *et al.*, 2015). Even though dissolution rate of aluminium in phosphoric acid medium is lower compared to the dissolution in hydrochloric or sulphuric acid medium, it does corrode aluminium and its alloys and its corrosion is not at all negligible (Fouda *et al*., 2012; Prabhu and Padmalatha, 2013). Therefore, it is necessary to use inhibitors for controlling the corrosion of aluminium in phosphoric acid solution during cleaning processes (Amin, 2009; Fouda *et al*., 2012; Prabhu and Rao, 2013).

Corrosion inhibitors are compounds that are added in small quantities to an environment to prevent corrosion of metals. Most of the efficient acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms in their molecule (Sastri, 1998; Mahmoud and Ahmed, 2006). Many synthetic organic compounds, such as triazole derivatives (Khaleed and Al-Qahtani, 2009), Schiff base (Ashassi-Sorkhabi, *et al*., 2006), pyridine derivatives (Kliskic *et al*., 1997), triazine derivatives (Wang, 2006) are effective corrosion inhibitors in acidic media. Unfortunately, the synthetic organic compounds cause damage to the environment, toxic to humans and other living organisms (Gece, 2011). In the past two decades the research in the field of green inhibitors has been addressed toward the goal of using cheap and effective with low environmental impact. In an attempt to find corrosion inhibitors that are environmentally safe, there has been a growing trend in the use of natural products such as products derived from plants, animals or minerals as corrosion inhibitors for aluminium in acid-cleaning process (Vargel, 2004; Ghulamullah *et al*., 2015). The reason for this is the presence of complex organic species such as tannins, polyphenols, alkaloids, carbohydrates and proteins as well as their acid hydrolysis products. Polyphenols, flavonoids and phenolic acids extracted from different plants have shown to have anticorrosive as well as antioxidant activity (Raja *et al*., 2008; Sangeetha *et al*., 2011). The use of these natural products is more effective and highly environmentally benign and harmless compared to organic and inorganic inhibitors used in chemical or any industrial applications (Obot *et al*., 2011; Prabhu *et al*., 2013; Sangeetha *et al*., 2013).

Aside from plants, honey is also a natural product reported to be good for retarding the corrosion rate of different types of materials in various environments (El-etre, 1998; Berkovic *et al*., 2008; Rosliza *et al*., 2010; Wan *et al*., 2011). Natural honey offers interesting possibilities for corrosion inhibition because it is safe, inexpensive, readily available and highly soluble in water (Berkovic *et al*., 2008; Rosliza, *et al*., 2010). Honey mainly consists of glucose and fructose but also contains amino acids, phenolic compounds, organic acids, vitamins, minerals, lipids, enzymes and other phytochemicals (Baltrusaityte *et al*., 2007; Silva *et al*., 2013). Similarly with plant extracts the polyphenolic compounds from honey are considered as one of the important groups of components identified in honey having anticorrosive activity. However, the use of stingless bee honey as a corrosion inhibitor for any metal or alloy has not been reported in the literature. Like natural or honey from natural honey, hundreds of bioactive substances have already been found in stingless bee honey from different species in different countries (Oddo *et al*., 2008; Silva *et al*., 2013). Among the compounds with biological activity that are present in stingless bee honey are the compounds that display antioxidant capacity, such as phenolic acids, flavonoids and the enzyme glucose oxidase and catalase (Aljadi and Kamaruddin, 2004). Thus, it was expected for stingless bee honey to have anticorrosive properties as shown by natural honey.

1.2 Problem statement

Corrosion inhibitors are widely used in industry to reduce the corrosion rate of aluminium and its alloys in contact with aggressive environment. The environmental toxicity of organic and synthetic corrosion inhibitors have prompted the search for eco-friendly corrosion inhibitors as they are biodegradable, do not contain heavy metals, ecologically acceptable, inexpensive, readily available and renewable. Most eco-friendly corrosion inhibitors are developed based on natural products such as plants or products derived from plants, animals and minerals. Although substantial research has been reported on the anti-corrosive of natural honey on aluminium, works on stingless bee honey have not been reported. Stingless bee honey contains polyphenolic compounds which have anti-corrosive activities.

1.3 Research objectives

The aim of this research is to determine the corrosion inhibition efficiency of stingless bee honey and its relationship to the phenolic contents and antioxidant activity. In order to achieve this aim, the research is divided into several objectives:

1. To determine the functional groups in stingless bee and natural honey to identify the functional group responsible for corrosion inhibition.

2. To determine the phenolic contents and antioxidant activity in both honeys.

3. To study the correlation between polyphenolic contents based on the total phenolic contents and antioxidant activity of both honeys on the corrosion inhibition of aluminium alloy in 1 M H_3PO_4 solution.

4. To determine the corrosion inhibition efficiency of both honeys on the aluminium alloys in 1 M H_3PO_4 solution by electrochemical and chemical methods as well as surface analysis.

5. To evaluate the thermodynamic aspects of inhibitors and adsorption corrosion inhibition of stingless bee honey on aluminium.

6. To propose the inhibition mechanism based on inhibitors adsorption profile.

CHAPTER TWO

LITERATURE REVIEW

2.1 Corrosion

Corrosion is the process of chemical or electrochemical reaction of metals and its alloys with the environment which causes a destructive effect (Eker and Yuksel, 2005; Ahmad, 2006). Corrosion process converts the refined metal to more stable oxide or salts (Manappallil, 2015; Reyes-Tovar, 2015). The degradation of the useful properties of materials and structures will occur due to the corrosion including strength, appearance and permeability to liquid and gases. The exposure to moisture in air caused many structural alloys to corrode. It may form a pit or crack onto the surface. Corrosion processes are responsible for many bad effects in the industrial process.

Prevention is the most practical way and achievable than complete elimination to prevent major accident due to corrosion problem. There are several accidents due to corrosion. In 1995, there was an explosion due to corrosion through processing chemicals at the Gaylord Chemical Corporation plant in Bogalusa, Louisiana. It was caused by a large reddish-brown vapour which was leaking due to corrosion and released from the tank (Dotson and Jones, 2005). There were also several accidents due to the pitting corrosion of aircraft and helicopters that may cause problems in our industry where around 1997, there was a serious incident caused by corrosion and pitting present in bell helicopter in stringer and fuselage (Hoeppner *et al*., 2000). In December 1967, the U.S. Highway 35 Bridge connecting Point Pleasant, West Virginia and Kanauga, Ohio suddenly collapsed into the Ohio

River. From the inspection and investigation from the researchers over the years, it was caused by the stress corrosion and corrosion fatigue which allowed the crack to grow and caused failure to the entire structure (LeRose, 2001). All this happened when the corrosion process was not prevented and minimized. These are the examples of the fatal accidents due to corrosion that have been reported.

There are several types of corrosion including wet corrosion and dry corrosion. Wet corrosion of metals occurs involving the process of oxidation and reduction through electron transfer (Einar, 2004). The oxidation process is the process of losing electron of the metal atoms as the surrounding environment gains the electrons in the reduction process. The cathode is metal, liquid or gas which gains the electrons whilst the metal where electrons are lost is called the anode. Dry corrosion occurs when there is no water or moisture to accelerate the corrosion process (Shreir, 2013). There are many factors that showed the corrosiveness of the environment. The amount of the oxygen or the presence of water and the moisture could greatly accelerate the rate of the corrosion (Martinez, 2012).

The components involved in the electrochemical corrosion cell are anode, cathode, electrolyte as well as the electrical conductor which is between the anode and cathode for the flow of the electric current (Steven, 2016). The electrons can flow through metal from the anodic to the cathode regions with the presence of the electrolyte in order to transport ions to or from the metal (Stephen, 2012). The corrosion will not occur when any of the components is absent.

2.2 Techniques in corrosion studies

2.2.1 Weight loss measurement

The weight loss method is well-known and also the simplest technique from all the corrosion monitoring techniques. This method involves exposing the specimen of the metal to the process of the environment in a certain time and finally removing the specimen for analysis (Doua’a, 2015). It is the basic method which is obtained from the weight loss of the specimen. The corrosion rate may be expressed as the weight loss taking place over the period of exposure. Several factors should be considered when the data is obtained. The factors are the size of the immersion metal, volume of the electrolyte and also the time of immersion (Aisha *et al.*, 2015). The corrosion rate is calculated in the unit millimetre per year (mm yr^{-1}) on the basis of the apparent surface area while the percentage inhibition efficiency (IE %) was calculated using Equation 2.7 (Tebbji *et al.*, 2011). The immersion time depends on the condition in the studies. There were several researches that used different immersion times such as 8 hours (Yiase, *et al.*, 2014), 3 days (El-Etre and Abdallah, 2000) and 60 days *(Wan, et al.*, 2011).

There are several advantages for the weight loss method. This technique is applicable to all environments and the weight loss may be readily determined and corrosion rate can be easily calculated. Inhibitor performance can also be easily assessed and corrosion deposits may be observed and also analysed.

2.2.2 Potentiodynamic polarization measurement

The phenomenon of corrosion may be explained in terms of the electrochemical reactions. Electrochemical technique should be used to study the phenomenon. The potentiodynamic polarization measurement is the characterization of the metal specimen by its current-potential relationship in aqueous environment. Passivation tendencies and effects of the inhibitors or the oxidizers on the specimen can be easily investigated with this method (Calderon *et al.*, 2015). Thus, the corrosion characteristic of the metals and alloys can be compared. This technique can provide significant useful information regarding the corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion in the designated environment. The term polarization is related to a shift or the change in potential which is caused by a flow of the current (Linda, 1994). The rate where the anodic or cathodic take place on the working electrode is the representation of the current.

Once a metal specimen is immersed in a corrosive medium, both the reduction and oxidation processes will happen on its surface. E_{corr} may be defined as a potential at which the rate of oxidation is exactly equal to the rate of reduction. It predominates at the expense of the cathodic current when the specimen is polarized slightly more positive than E_{corr} (Zhila, 2015). Obviously, if the specimen is polarized in the negative direction, the cathodic current predominates and the anodic component becomes negligible.

There are three important electrodes in this technique which are the working electrode, an auxiliary electrode and a saturated calomel reference electrode. The Tafel plot (Figure 2.1) is done on the metal specimen by polarizing the specimen about 250 mV anodically and cathodically from the corrosion potential, E_{corr}. The potential scan rate can be 0.1 – 1.0 mVs^{-1}. It relates to the potential change with time. Then, from the extrapolating linear portion of the curve to E_{corr} of Tafel plot, the corrosion current i_{corr} is obtained (Shetty *et al.*, 2016).

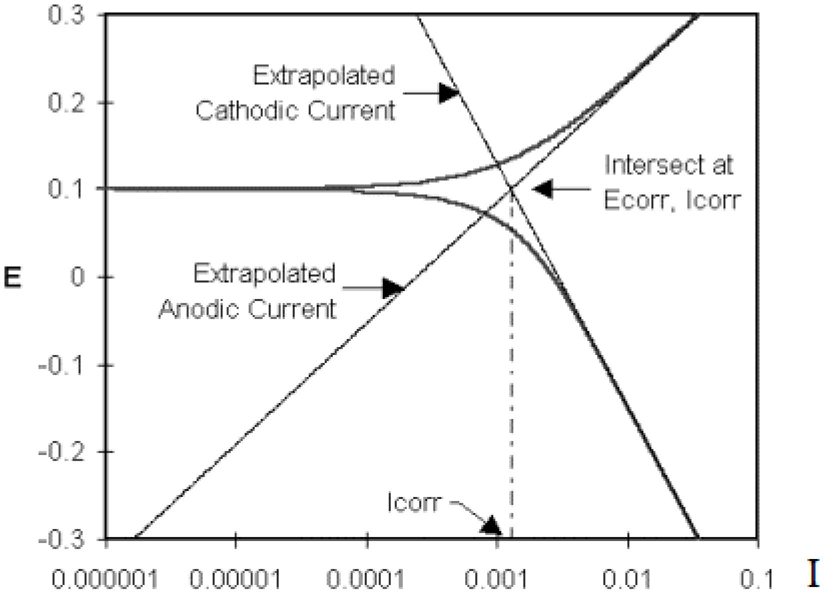

Figure 2.1: Tafel plot (Zaki, 2006)

The parameters in the potentiodynamic polarization method are the corrosion potential, E_{corr}, the corrosion current, i_{corr}, the anodic and cathodic Tafel constant (β_a and β_c) and corrosion rate (CR). Corrosion rate is defined as the rate of the metal surface to be corroded. The corrosion rate can be calculated by using this equation:

$$Corrosion\ Rate\ (mpy) = \frac{0.13 \times i_{corr} \times M_{ew}}{\rho} \tag{2.1}$$

Where i_{corr} ($\mu A\ cm^{-2}$) is the corrosion current density, ρ ($g\ cm^{-3}$) is the density of the corroding metal and M_{ew} (g) is the equivalent weight of the corroding metal.

2.2.3 Electrochemical impedance spectroscopy (EIS) measurement

EIS measurement is the other method to evaluate and investigate corrosion inhibition. This measurement is the laboratory technique to know about the mechanism for electrochemical reaction and to investigate the passive surface (Pieterse, 2014). This technique is usually measured by applying an AC potential to an electrochemical cell and measuring the current through the cell. It is a technique where a small amplitude signal with voltage between 5 to 50 mV is applied to the specimen over the range of frequencies (Popkirov *et al.*, 1995). The frequency range for the corrosion system is usually from 0.001 Hz to 100 kHz.

The important part of this analysis is to create an equivalent circuit for the system. The interpretation of the electrochemical response is usually in terms of an equivalent circuit (Zelinka *et al.*, 2009). The common electrochemical circuit is used to describe a metal or the electrolyte interface (Figure 2.2). As the linear polarization method is valuable for bare metals in many situations, it is deficient for metals that are coated with the electricity insulating material and for bare metals which is when the electrolyte is not very conductive. This problems may solve by EIS method.

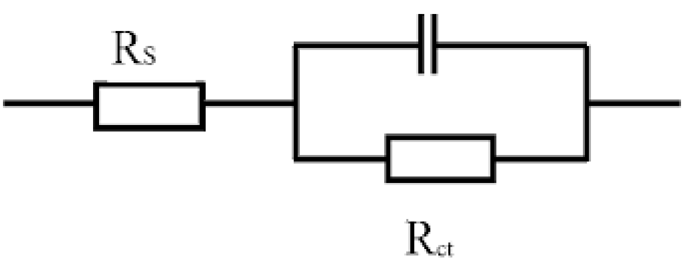

Figure 2.2: Equivalent circuit

From the figure above, there are three main electrical components which are represented by R_s, R_p, and C_{dl}. The relationship between R_p and C_{dl} is when the inhibitor concentration increases thus the polarization resistance, R_p will also increase and double layer capacitance, C_{dl} will decrease. Therefore, the inhibition efficiency obtained will increase. The decreasing of the C_{dl} may be interpreted as the adsorption of inhibitor onto the electrode surface. R_p is always inversely proportional to the corrosion current density i_{corrr}. It can be seen through the Stern-Geary relation (Song and Saraswathy, 2007) as follows:

$$i_{corr} = \frac{1}{R_p\,(\frac{\beta a \beta c}{2.303\,(\beta_a + \beta_c)})} \tag{2.2}$$

Where β_a and β_c is the anodic and cathodic Tafel slopes respectively.

Generally, EIS spectra are plotted in Bode and Nyquist diagrams. For Nyquist diagram, $-Z_{imaginary}$ is plotted against Z_{real} and frequency is contained implicitly. A typical Nyquist plot (Figure 2.3) is known as a complex impedance plane plot. It shows imaginary versus real impedance component. The resulting semi-circle will appear on the plot. The solution resistance is read by extrapolating semicircle toward the left. Then, polarization resistance will be read from the extrapolation semicircle toward the right (Dawib, 2013). In the Nyquist plot, the impedance can be represented as a vector of length |Z|. The angle between this vector and the x-axis is ϕ. The value of parameters such as $R_{s,}$ R_p and C_{dl} may be obtained by using the equation below:

$$Z = \frac{R_s + R_p}{1 + j_\omega C_{dl} R_p} \tag{2.3}$$

Where R_s is the solution resistance, R_p is the polarization resistance and is also known as R_{ct} for charge transfer and lastly C_{dl} is double layer capacitance. The difference between R_s and $R_s + R_p$ shows the magnitude of resistance of corrosion.

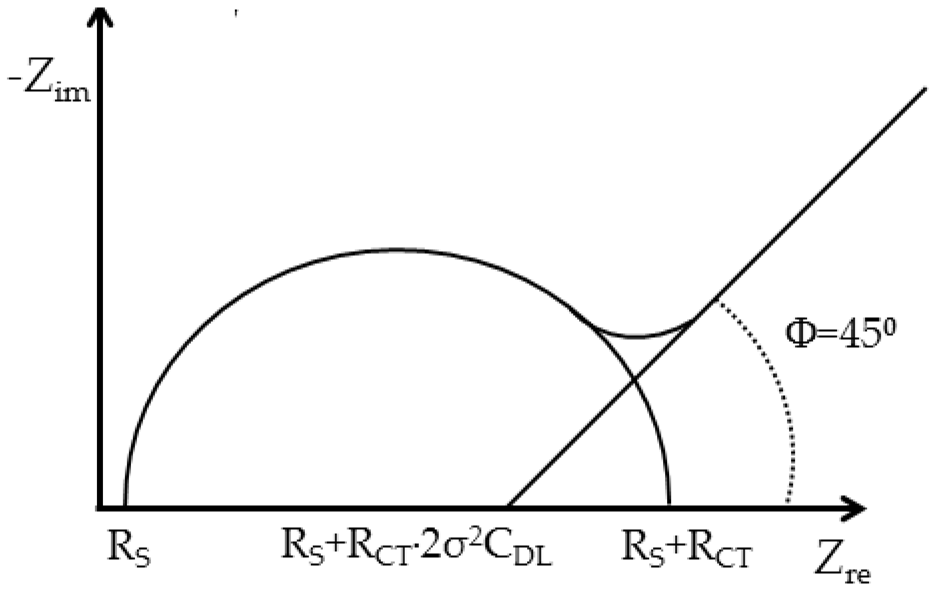

Figure 2.3: Nyquist plot (Kaesche, 2012)

For Bode diagram (Figure 2.4), the impedance is plotted with log frequency on the x-axis and both absolute values of impedance and phase shift on y-axis. The Bode plot yields value of R_s and $R_p + R_s$. From the high frequency horizontal plateau, the solution resistance is obtained whilst the polarization resistance may be determined at low frequency. Lastly, the curve represents a straight line with slop of -1 at intermediate frequency. The double layer capacitance, C_{dl} is determined by extrapolating this line to y-axis.

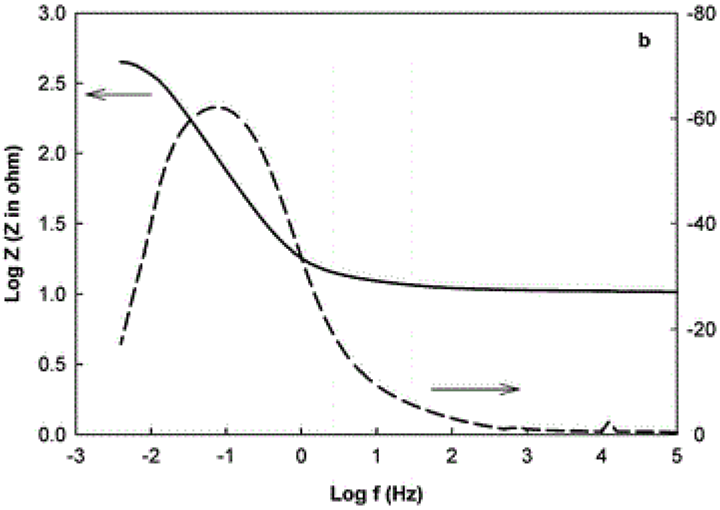

Figure 2.4: Bode plot (Zaki, 2006)

2.2.4 Pitting corrosion

Pitting corrosion is the important problem which is the root of many corrosion failures. The surface of the metal is being attacked in small localized area in the pitting corrosion. The effect from the pitting corrosion is marked even though very little metal is removed from the pitting corrosion. The metals or alloys which are exposed to the solution containing aggressive anions, will result in the pitting corrosion. It leads to the formation of cavities or holes. The pitting corrosion may be formed through chemistry of the environment as well as the leading condition (Loto, 2013).

The potential characteristics are found from the electrochemical studies of the pitting corrosion. The technique of the cyclic polarization is for the measurement of the pitting tendencies of a specimen in a given metal-solution system. Stable pits are formed at the noble potential which is lower than pitting potential E_{pit} to the repassivation potential E_{rp}. In the cyclic polarization experiment, the potential limit above which the formation of pitting begins represents E_{pit} while for E_{rp} refers to the limit below which the metal remains passive. E_{rp} was the potential which the forward and reverse scan cross. The size of the pitting loop is a rough indication of pitting tendency. The tendency to pit is larger when the loop is larger (Frankel, 1998).

2.3 Corrosion of aluminium

Aluminium is a metal with good electrical and thermal conductivity despite the lightweight with density of 2.71 g cm^{-3} (Gerengi, *et al.*, 2014). At present, aluminium and its alloy are widely used in many applications such as in the field of automotive, aerospace, food handling, construction, electrical transmission, and heat exchange (Oki, *et al* 2013; Fouda, *et al* 2014; Al-Mhyawi, 2014). Pure aluminium had also been known as too soft to be used as a heavy duty material for large structures. Even though it is too soft, high strength aluminium alloys can be transformed by adding appropriate alloying elements such as silicon, copper, magnesium and zinc (Ghoneim, *et al.*, 2012). Aluminium is always alloyed as it improves the mechanical properties especially when tempered. Physically, aluminium is a relatively soft, durable, ductile and lightweight metal with appearance ranging from silvery to dull grey in colour which also depends on the surface roughness. Despite of all the properties, it is also nonmagnetic and does not easily ignite. Aluminium is also recyclable which has substantial scrap value and well established market for recycling, providing for both economic and environmental benefits (Davis, 1999). Chemically, aluminium resists corrosion due to the thin surface layer of aluminium oxide that is formed when it is exposed to the air. Unfortunately, in highly acidic solutions, the passivation layer can be destroyed and corrosion takes place. Thus, corrosion studies of aluminium and aluminium alloys get so many attention by researchers because it will affect the importance of technologies and also industrial applications (Ameer, *et al*., 2012; Hassan and Zaafarany, 2013; Sangeetha, *et al*., 2013; Chaubey, *et al*., 2015).

Electrochemical is the reaction which depends on the transfer of electrons from the anode where aluminium is dissolving and releasing electron and the cathode where the electrons are consumed. Any corrosion reaction in aqueous solution will involve oxidation of the metal and also reduction of the species of solution as a result of the transfer of electron between both reactants. The Al^{3+} ions are released from the anode through oxidation while the OH^- ions is formed where oxygen is reduced at the cathode. Al and H_2O are converted into ions Al^{3+} and OH^-, respectively which will react together to form an $Al(OH)_3$ deposit. It is the result of white powder or gel formed locally on the surface of aluminium alloy. Further destruction of the protective oxide film at the surface is due to the production of the H_2.

Anodic reaction:

$$Al\ (s) \longrightarrow Al^{3+}\ (aq) + 3e^- \qquad (2.4)$$

Cathodic reaction:

$$\frac{3}{2}H_2O\ (l) + \frac{3}{4}O_2\ (g) + 3e^- \longrightarrow 3OH^-\ (aq) \qquad (2.5)$$

The cathodic reaction represented by Equation 2.4 exemplifies corrosion in natural environment where corrosion occurs at nearly neutral pH values. In acidic solution, the cathodic reaction is (Salah *et al.*, 2012):

$$3H^{+}\,(aq) + 3e^{-} \longrightarrow \tfrac{3}{2}H_2\,(g) \qquad (2.6)$$

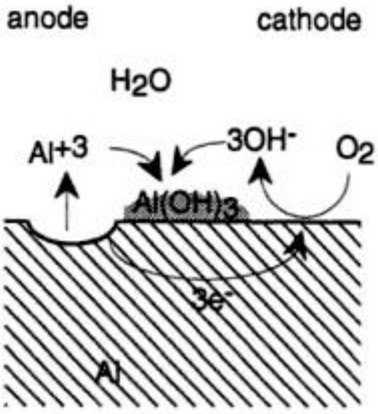

Figure 2.5: Electrochemical mechanism of corrosion aluminium (Mainier *et al.*, 2014).

The electrons transfer through the metal to the cathode. The combination between aluminium cation and the hydroxyl anion in the liquid will produce solid precipitate as in Figure 2.5. Once both anodic and cathodic partial reaction combines, the aluminium hydroxide is obtained (Equation 2.7 and 2.8). As a result, the white crystalline corrosion product powder will be formed and found on the surface of aluminium.

$$Al^{3+}\,(aq) + 3OH^{-}\,(aq) \longrightarrow Al(OH)_3\,(s)\downarrow \qquad (2.7)$$

$$Al^{3+}(aq)+3H_2O(l) \longrightarrow H^{+}(aq)+Al(OH)_3(s)\downarrow \qquad (2.8)$$

Hydrogen ions are consumed by the process. The pH in the droplet rises as the aluminium corrodes. Then, hydroxide ions (OH^-) appear in water as the hydrogen ion concentration falls. Next, they react with aluminium ions to produce insoluble aluminium hydroxide or green rust.

2.3.1 Corrosion of aluminium in phosphorus acid

Phosphoric acid, H_3PO_4, is colourless, odourless and also non- volatile with the syrup consistency solution and also known as orthophosphoric acid and phosphoric (V) acid. It is one of the major industrial chemicals which is widely used for the preparation of semiconductors and printed circuit board and also as the cleaning section in industry (Bank, 1997) . Despite that, H_3PO_4 is also used to remove mineral deposits from the process equipment and boilers. Other than that, it is being used for acid pickling and electro-polishing of aluminium (Amin, *et al.*, 2009). In the industrial applications, H_3PO_4 is used in the metal treatment. In metal treatment, purified phosphoric acid and phosphates are used in the process which is phosphating metal surface. It is to insulate them electrically and encourages paint to adhere to the treated surface. Furthermore, H_3PO_4 is also used in water treatment to prevent the deposition of lime scale and control the pH of water (Haman, 2015). H_3PO_4 which is a weak acid towards aluminium and its alloy has strong corrosiveness. Due to the strong corrosiveness on aluminium and their alloy, it is necessary to choose the right methods to control the corrosion of aluminium and also aluminium alloy in the H_3PO_4 solution. Nowadays, the protection of metals against the corrosion is a popular topic among researchers and receives great attention to prevent bad effects in the industry.

2.4 Corrosion protection

Corrosion protection is a method or technique to control the corrosion of a metal surface. It protects and minimizes the stage of corrosion which is commonly used for steel, fuel pipelines, tanks, ships and offshore oil platform. The cost and also the effectiveness of the method chosen to be used should be considered. There are many alternatives to prevent and minimize corrosion. Generally, there are several methods for controlling corrosion which involve the application of good design, materials selection, usage of protection of cathodic and anodic, application of protective coating layer and also by using corrosion inhibitors (Garverick, 1994). The corrosion protection can be minimized by using the proper design which include the material selection, drainage and also the access for maintenance. All the factors to get the proper design might prevent the corrosion and will minimize corrosion problem.

Other than that, selecting the material is one of the important methods that can prevent corrosion (Benjamin *et al*., 2006). Each industry has different material selection processes. Thus, with good and proper selecting material the corrosion protection will be essential for a long term. Next, cathodic protection is a more effective method to resist corrosion. For this protection, it requires changing the electrode potential of the metallic article or structure (Graeme, 2005). Therefore, the base metal is ensured to become the cathodic element of the circuit. Anodic protection is a potential-control electrochemical technique which usually prevents corrosion of the metal in the strong acidic or alkaline environment (Edeleanu, 1960).

The other method to prevent corrosion is by applying a coating layer to the metal. It is called barrier protection which is the oldest and most widely used corrosion protection method. The protection will act by isolating the base metal from the environment such as paints, the hot-dip galvanized coating which is barrier protecting the metal (Francis, 2010). It works by coating the metal with a protective coating that forms a tight barrier to prevent exposure to oxygen, water and salt (Popoola *et al*., 2014). Better protection occurs when the permeability of the coating system to the water is lower. The metal is protected as long as the barrier prevents corrosion. However, corrosion will begin when the barrier is breached.

Corrosion inhibitors are either organic or inorganic chemicals, formulations that are added only in a small quantity to the corrosive environment to reduce corrosion process on the protected surface. There are several matters to be considered to choose the corrosion inhibitors. The inhibitors must have the ability to reduce the corrosion rates. Lastly, it must not have side effects especially to the environment and become environmentally friendly corrosion inhibitor.

2.5 Corrosion inhibitor

In the industry, corrosion is one of the problems that should be solved. This phenomenon must be controlled to prevent accidents or bad effects. Corrosion inhibitors are compounds that will decrease the corrosion rate of the material typically a metal or an alloy when it is combined with a liquid or gas (Anbarasi, *et al*., 2013). Generally, inhibitors are substances or mixtures that may prevent or minimize the corrosion with low concentration and in aggressive inhibited environment. Preventing corrosive substance to the metal involves the mechanism for inhibiting corrosion which is usually through the formation of coating often a passivation layer. The corrosion rate can be reduced through adsorption of molecules onto the metal surface (Peme, *et al*., 2015). It can also be reduced by decreasing the diffusion rate for reactants to the surface of the metal. The electrical resistance of the metal surface should be increased to decrease corrosion rate. There are many factors to be considered when choosing an inhibitor such as cost and amount, availability and most importantly, it is safe to the environment. However, at present, many corrosion inhibitors show secondary effects that will damage the environment. Thus, the research community began searching for friendly environmentally friendly inhibitors such as organic inhibitors (Rani *et al*., 2012; Palou *et al*., 2014).

In the mechanism of the inhibitor, the inhibitor is chemically adsorbed onto the surface of the metal and will form a protective thin film. It will lead to the formation of a film by the oxide protection of the base metal. Many systems and commercial applications use inhibitors such as in cooling system, water processing, paints, oil and gas production units and refinery units (Saji, 2010). The development of corrosion inhibitor technology is widely used since the 1950’s and 1960’s (Sheeja, 2016). However, some of the inhibitors have high toxicity which is related to the bad environmental effects and health problems. Due to these reasons, strict international laws were imposed and the corrosion inhibitor must be reduced. Thus, researchers develop organic inhibitors which are environmentally friendly.

2.5.1 Types of inhibitors

Corrosion inhibitors can be classified according to the types of materials to be protected. For example in the oil refining processes, it must be of special interest for carbon steel which has a major component of iron. It must also inhibit copper-zinc alloys which is the most common materials used in the design of refineries (Aliofkhazraei, 2014). Other than that, corrosion inhibitors can be classified as anodic and cathodic inhibitors. Anodic inhibitors inhibit oxidation of the metal while cathodic inhibitors inhibit the reduction of oxygen and hydrogen. Both processes represent mixed inhibitors. Lastly, it can be categorized according to the types of compound that forms the active ingredient in the formulation which is inorganic or organic corrosion inhibitors. There are various organic and inorganic inhibitors such as molybdates, phosphonates, silicates and triazoles (Antonijevic and Petrovic, 2008).

Inorganic inhibitors are the ones that have active substance of inorganic compound. Application of organic compounds and natural products as corrosion inhibitors are the best alternative to the more toxic inorganic compounds (Ghulamullah *et al*., 2015). Chromium is example of the inorganic inhibitor which widely used as a potential corrosion inhibitor due to their higher efficiency (McCafferty, 1979, 1989). In spite of their advantage as corrosion inhibitor, chromates exhibit high toxicity and it is prohibited to be used in industrial application in high amount (Kesavan *et al*., 2012).

Organic inhibitor is a compound that has large molecular weight with the presence of heteroatom group. The examples of heteroatom group are nitrogen, oxygen, and also sulphur. Organic inhibitors which are from the flavonoids, alkaloids and other natural products obtained from natural sources like plants is called as natural organic inhibitors. The natural organic inhibitors are also efficient for metal corrosion inhibition. It all depends on the metals, the electrolyte used and also the types of plants itself. The examples of the natural organic inhibitors are natural honey (El-Etre and Abdallah, 2000), *Lupinous albus L*. (Abdel-Gaber *et al*., 2009), artemisia oil (Benabdellah *et al*., 2006), lawsonia (El-Etre *et al*., 2005), *Papaia, Poinciana pulcherrima, Cassia occidentalis* and *Datura stramonium* seeds (Zucchi and Mashi, 1985), *Delonix regia* extract (Abiola *et al*., 2007) and *Ocimum basilicum* extract (Oguzie *et al*., 2006). Other than that, some organic inhibitors also include synthetic compound with negligible toxicity. Synthetic organic inhibitor is capable of bringing harm to the environment by the toxicity (Wan *et al.*, 2011). Most of them are highly toxic which may cause bad impact to human and also the environment. From previous researches, there are many examples of synthetic compound which are used as an inhibitor such as indole derivatives (Dudukcu *et al.*, 2004), 2-hydrazino-6-methyl-benzothiazole (Ajmal *et al.*, 1994), thiophene derivatives (Galal *et al.*, 2005), hexadecyl pyridinium bromide (HPB) and hexadecyl trimethyl ammonium bromide (HTAB) (El-Maksoud, 2004), polyaniline and poly (o-methoxyaniline) (Kilmartin *et al.*, 2002) and 2,5-bis(n-methoxyphenyl)-1,3,4-oxadiazoles (Bentiss *et al.*, 2002).

Due to the bad effect towards the environment, the researchers now focus on the environmentally friendly corrosion inhibitors. From the view point of economic and the environment, the natural product and plant extracts are an excellent alternative as inhibitors due to the biodegradability and availability. The inhibitor is efficient due to its compatibility with the environment, economical for application and can produce the desired effect when presented in small concentrations. The inhibitor efficiency ($IE\ \%$) can be measured with the given equation (Taleb *et al.*, 2011) :

$$IE\ \% = \left(\frac{W_o - W}{W_o}\right) \times 100 \tag{2.9}$$

Where W_o is the corrosion rate in the absence of inhibitor while W is the corrosion rate in the presence of inhibitor.

2.6 Adsorption process

In recent years, the development of the natural organic inhibitors becomes popular among researchers due to the eco-friendly effect especially to the environment. The important process for the chemical reaction is the process of adsorption. The process of adsorption on metal surface is through blocking the active sites by displacing water molecules and forming a compact barrier film which is to decrease the corrosion rate (Obot and Obi-Egbedi, 2010). According to Ahamad and Quraishi (2009), the adsorption of inhibitors on metal or solution interface is influenced by the nature and surface charge of metal, the type of the aggressive electrolyte and chemical structure of the inhibitors.

The process that involves charge sharing or charge transfer between the inhibitor molecules and the metal surface is called chemisorption. It is a slow reaction compared to the physical adsorption (Al-Azzawi and Hammud, 2014). The electron transfer is typical for the transition metal that has low energy electron orbitals. In the chemisorption, electron will be transferred by the compounds that have relatively loose band electrons. Chemisorption is the most effective process rather than physically adsorbed. As the temperature increases, adsorption and inhibition will decrease. It is also specifically but not completely reversible (Sastri, 1998).

Physically adsorbed inhibitors will interact rapidly but they are easily removed from the surface. This adsorption is caused by the electrostatic force which exists between ionic charges or dipoles on inhibitor. Physisorption is also caused by the electrostatic charge at the metal surface. Generally, the electrostatic adsorption force is relatively weak and has low activation energy. The increase in temperature will facilitate desorption of physically adsorbed inhibitor molecules. The molecules of water will be adsorbed to the metal surface which is immersed in an aqueous