

**CORROSION INHIBITION BY HENNA
LEAVES EXTRACT IN INDUSTRIAL
WASTEWATER**

NUR AFRINA BINTI KAMARUL BAHRIN

B. ENG(HONS.) CIVIL ENGINEERING

UNIVERSITI MALAYSIA PAHANG

UNIVERSITI MALAYSIA PAHANG

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ID Number : AA15113

Date : 31 MAY 2019

CORROSION INHIBITION BY HENNA LEAVES EXTRACT IN INDUSTRIAL
WASTEWATER

NUR AFRINA BINTI KAMARUL BAHRI

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ABSTRAK

Inhibitor korosi adalah sebatian kimia yang ditambah kepada air sisa industri untuk mengurangkan kadar kakisan. Ia boleh memperlahankan serangan kakisan asid ke arah tiub, paip gerudi dan sebarang logam lain yang dihubungkan dengan asid semasa rawatan. Walau bagaimanapun, kos menggunakan inhibitor kakisan adalah mahal. Oleh itu, penyelesaian masalah ini adalah dengan menggunakan ekstrak tumbuhan sebagai perencat kakisan. Kajian ini bertujuan untuk menentukan dos optimum inhibitor pada keluli dan kesan suhu dan masa terhadap keluli dalam 1M HCl. Kesan penghambatan kakisan ekstrak daun inai (*Lawsonia inermis*) pada keluli dalam 1 M HCl telah dikaji dengan kaedah penurunan berat keluli. Eksperimen dijalankan pada 25 °C, 40 °C, 50 °C, 60 °C, dan suhu bilik dengan kepekatan ekstrak daun inai yang berbeza. Masa rendaman adalah 4 minggu untuk mengira kecekapan perencatan. Kecekapan tertinggi adalah 6% yang berada pada kepekatan daun inai ialah 35g/L. Untuk kadar kakisan, pembacaan tidak sekata di mana pada 5g/L kepekatan, kadar kakisan berkurangan. Dos optimum daripada daun henna ekstrak untuk kecekapan perencat ialah 35g/L. Untuk kesan suhu, apabila suhu meningkat, kecekapan inhibitor juga meningkat. Ia boleh dibandingkan apabila konsentrasi perencat adalah 35g/L, kecekapan perencatan adalah lebih rendah (1.84%) pada 25 °C berbanding suhu pada 60 °C iaitu 6.29%. Untuk perbezaan masa, ia mempunyai bacaan kecekapan hambatan tertinggi pada minggu keempat. Ketika pada minggu keempat, kecekapan inhibisi adalah 6.29% manakala pada minggu pertama, kecekapan inhibisi adalah 4.08%. Bagi isotherm penjerapan, graf Langmuir menunjukkan bahawa penjerapan ekstrak daun inai (*Lawsonia inermis*) mematuhi isotherm adsorpsi Langmuir. Sebagai kesimpulan, daun Henna boleh digunakan untuk mengurangkan hakisan peralatan dalam air sisa industri. Ia juga mempunyai kecenderungan untuk menjadi inhibitor yang baik. Dengan menggunakan daun henna, ia dapat mengawal dan mengurangkan kakisan di mana ia dapat mengurangkan kos.

ABSTRACT

A corrosion inhibitor is a chemical compound which added to industrial wastewater in order to reduce the rate of corrosion. It can slows the attack of acid corrosion towards tubing, drill pipe and any other metals that contact with acid during treatment. However, the cost of using corrosion inhibitor is expensive. Therefore, the solution of this problem is by using plant extract as corrosion inhibitor. This study aims to determine the optimum dosage of inhibitor on mild steel in 1M HCl and the effect of temperature and contact time on mild steel in 1M HCl. Corrosion inhibition effect of Henna Leaves Extract (*Lawsonia inermis*) on mild steel in 1 M HCl has been investigated by weight loss method. Experiments will be conducted at 25°C, 40°C, 50°C, 60°C, and at room temperature with different concentration of henna leaves extract. The immersion time is 4 weeks to calculate the inhibition efficiency. The highest efficiency is 6% which is at the concentration of henna leaves is 35g/L. For rate of corrosion, the reading is unmanufactured where at 5g/L of concentration, the rate of corrosion is decreased. The optimum dosage of henna leaves extract for efficiency of inhibitor was 35g/L. As for the effect of temperature, when the temperature was increased, the inhibition efficiency also increased. It can be compared that when the concentration of inhibitor is 35g/L, the inhibition efficiency was lower (1.84%) at 25°C compared to the temperature at 60°C which is 6.29%. For the contact time, it have the highest inhibition efficiency reading at the fourth week. When at the fourth week, the inhibition efficiency is 6.29% while at the first week, the inhibition efficiency is 4.08%. For the adsorption isotherms, the Langmuir graph shows that the adsorption of henna leaves extract (*Lawsonia inermis*) obeys Langmuir adsorption isotherm. As a conclusion, Henna leaves can be used in reduce the corrosion of equipments in industrial wastewater. It also has the tendency to be a good inhibitor. By using henna leaves, it can control and reduce the corrosion where it can reduce the cost.

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LIST OF SYMBOLS

%	Percentage
°C	Degree Celcius
M	Molarity
mL	Millilitre
K	Kelvin
g/L	Gram per Litre
mg/L	Milligram per Litre

LIST OF ABBREVIATIONS

NACE	National Association of Corrosion Engineers
HCl	Hydrochloric Acid
SCC	Stress Corrosion Cracking
VCI	Volatile Corrosion Inhibitor

CHAPTER 1

INTRODUCTION

1.1 Preamble

Corrosion is a natural phenomenon where it happens in many situations. This is because it can happen when a chemical reaction is reacted between metal, air and the surrounding environment. The process of corrosion is not only depends on the chemical properties of metal but it also influence the changes of mechanical behaviour and physical properties of the metal. The name of the reaction of corrosion process is reduction-oxidation (redox) reaction where some species of metal is required oxidized and some species is reduced. In industries, corroded metal causes major losses due to the wide application of metals (Arockiasamy *et al.*, 2014).

There are three methods that used commonly in industry to control and protect the metal from corrosion. The methods are coating, cathodic protection and corrosion inhibitor. For coating, there are various types of coatings that are used in industrial waste which are physical barrier coatings, metallic coatings, non-metallic coatings and chemical conversional coatings. These coatings provide a barrier between the surface and the environment (Singh *et al.*, 2012). Most of the steel pipes are highly corrosive nature of wastewater where the coatings are cracks and develop small pinholes. The other treatment that can prevent from corrosion is cathodic protection.

Cathodic protection is to control the corrosion of the piping and tanks where the system is been tested by National Association of Corrosion Engineers (NACE)-certified specialist (Camila *et al.*, 2014). Corrosion inhibitor is a chemical compound where to decrease the rate of corrosion of material which are steel and metal. Inhibitors are act through the process of surface adsorption and its adsorption depends on the nature and

surface charges on the metal (Pavithra *et al.*, 2013). To prevent the access of corrosive substance to metal, the formation of coating is involved in the mechanism of corrosion inhibition. Inorganic inhibitors, which are mainly oxidizing agents, such as chromates, iodates, and tungstate act as anodic inhibitors and their metallic atoms are enclosed in the film improving its corrosion resistance. However, these compounds are very expensive (Kumar *et al.*, 2018).

Although many of these tested compounds have high inhibition efficiency, the usage of them still undesired due to their adverse effect on human, environment, as well of their high cost. The increasing concern about these problems had attracted industries to replace it with more environmentally acceptable, readily available and renewable source for wide range of inhibitors which have rich source of ingredients and high inhibition efficiency.

1.2 Problem Statement

Corrosion is always happen in industrial wastewater equipments such as pipes, tanks and pumps. There are many solutions that have been discovered to reduce the corrosion in the equipments. The method that used to retard the process of corrosion is anticorrosive coatings. Inorganic pigments are usually added to coatings for long term performance where can release the corrosion inhibiting (Zulkifli *et al.*, 2017).

Besides that, the method that used to prevent corrosion is cathodic protection system. Before install this system, an economic evaluation should be conduct where the cost of the system is low but it is difficult to quantify from the failures of equipment. However, they are giving effect to environment and health where it due to carcinogenic nature and toxic from the corrosion inhibitors. Umoren *et al.*, (2018), illustrated that nitrogen based organic inhibitors like amines and imidazolines or their salts are the most profitably used to occur the corrosion in internal pipelines. Due to their toxic nature, they are not environmentally friendly and it is very costly even though the inhibitors have good protection and stable in corrosive environments (Umoren *et al.*, 2018).

Hence, to reduce the cost and the effect on environment and health, the cheaper and organic inhibitor have been found. The most common method that been used to prevent the corrosion in wastewater treatment plant are very difficult to qualify. Therefore, the aim of this research is to find the best inhibitor to prevent the corrosion of metal in wastewater treatment plant.

1.3 Objective of Study

There are two objectives for this research based on the problem statement. The following are the objectives:

- i. To determine the optimum concentration of inhibitor
- ii. To compare the effect of contact time and temperature of inhibitor

1.4 Scope of Study

This study carried out to study the optimum dosage of the inhibitor to prevent the corrosion and the effect of contact time and temperature of inhibitor on mild steel. Henna leaves have been collected from the person who have henna trees. Henna leaves extract was prepared at laboratory. HCl solution was prepared where this solution was presented as industrial wastewater. This study was focusing the effectiveness of henna leaves extract as the corrosion inhibitor to prevent the corrosion happen in industrial wastewater.

1.5 Significance of Study

This research was do the treatment which can prevent the corrosion of the equipments such as pipes, tanks and pumps. The inhibitor that used in this study is organic leaves. By using organic leaves, it can reduce cost, improve the efficiency, eco environmental and provide variation methods of the industrial wastewater. From this study, it become another alternative which can reduce the cost of conventional treatment. This study is to determine the efficiency of the inhibitor where it can prevent the metal from corrosion. End of this study, the method of lower cost and effectiveness of inhibitor is proposed. This treatment can be used widely by industrial management where it can control and reduce the corrosion of metal.

CHAPTER 2

LITERATURE REVIEW

2.1 Corrosion

Corrosion is the major problem in industry where most of the equipment is used from steel and aluminium. This problem is the one major loss to industry where they need to repair and cost billion per year in one state. This problem occur when the metal react between air and surrounding environment. In industries sector, they used mild steel widely as constitutional material because it is a good mechanical property and low cost. However, by using mild steel, the main problem is occur where the dissolution is in acidic medium (Chaudhari *et al.*, 2016)

Corrosion also means the breaking down of essential properties in a material due to chemical reactions with its surroundings. This means that a loss of electrons of metals reacting with water and oxygen (Abeng *et al.*, 2017). Weakening of iron due to oxidation of the iron atoms is a well-known as an example of electrochemical corrosion. It also known as rusting. This type of damage produces oxide or salt of the metal (Abeng *et al.*, 2017). It also can refer the degradation of ceramic materials as well as the discoloration and weakening the polymers by the sun's ultraviolet light.

Most structural alloys corrode merely from exposure to moisture in the air. However, the process can be strongly affected by exposure to certain substances. Corrosion also can form a pit or crack. It also can extend across a wide area to produce general deterioration. There are some general causes of corrosion in industry. They cause from the electrochemical reactions that follow thermodynamics law. It is to establish the rate of corrosion or the reactions that affected by corrodent concentrations and ion.

The most common form of corrosion is in aqueous solutions like seawater, water and others medium that also provide aqueous forms. The speed of corrosion can increase when the impurities help in setting up the voltaic cells. The higher reactivity of metal, the higher possible the metal can corrode. Next, the presence of electrolyte and carbon dioxide can increase the rate of corrosion. Lastly, at higher temperature, the corrosion also can be increase. To reduce the corrosion, there are some efforts that have be done such as less predictable forms, less visible damage and controlled corrosion treatments (Fouda *et al.*, 2015). The example of controlled corrosion treatments are passivation and chromate-conversion which can increase a material's corrosion resistance.

2.1.1 Cost of Corrosion

The total national yearly cost of metallic corrosion in the United States was estimated at \$275 billion, or 3.1% of the U.S. gross domestic product (GDP) of \$8790 billion, in 1998 (Gysbers *et al.*, 2016). This total includes the replacement costs and lost production costs as well as the decrease in lifetime and the expected replacement value of a given component subject to damage by corrosion. NACE International today has released the "International Measures of Prevention, Application and Economics of Corrosion Technology (IMPACT) study where it can estimates the total global cost of corrosion. From the study, the cost of corrosion can be US\$2.5 trillion which roughly equivalent to 3.4 percent of the global Gross Domestic Product (GDP). In conference on 2016 in Vancouver, it already examined the economics of corrosion and the corrosion role of management in established the best practices in industry. It also found that the implementing of the corrosion towards prevention is the best practice to save the global which is between 15-35% of the cost of damage.

CEO of NACE International reported that the IMPACT study needs to have a change in how to decrease the corrosion problems in industry. NACE International need to take responsibilities about the corrosion problems in pipeline or water treatment plant in order to avoid the catastrophic events (Gysbers *et al.*, 2016). IMPACT also assessed the corrosion management practices towards the various industries and regions which specific in pipeline, drinking and wastewater industries. It also provide the training and professional development which have tens of thousands of engineers and professionals in more than 130 countries. However, industry need more programs for academics and

more universal of communications for all levels. The cost of corrosion also includes the means where the effects of corrosion mitigated, for example, use of cathodic protection, inhibitors, and alternative materials of construction, overdesign and protective coatings. Figure 2.1 shows the direct cost or losses in United States while Figure 2.2 shows corrosion cost distribution in US or Japan.

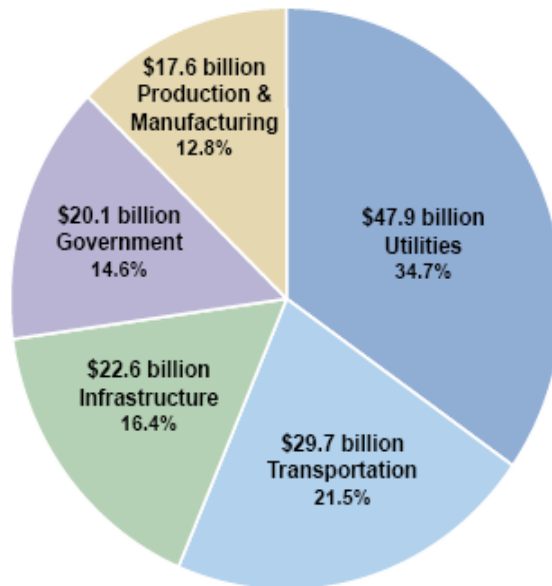


Figure 2.1 Direct Cost or Losses in United States

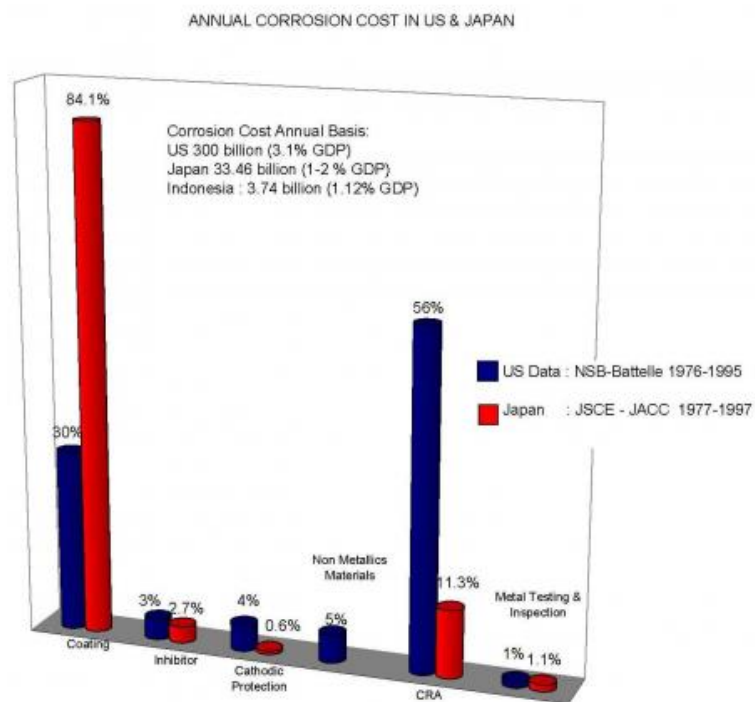


Figure 2.2 Corrosion cost distribution in US or Japan

2.2 Type of Corrosion

There are various forms of corrosion that happened in industry. It can be separated into two types of distinct which are generalized and localized. Generalized corrosion is affect of the entire surface area of an asset where it can formed of a more or less uniform loss of surface material or a generalized thinning. It is a spans the entirety of a metal surface. Generalized corrosion is treatable, predictable and easy to detect where it is widely regarded as the less treacherous of the two types of general corrosion. The metal surfaces that affected by generalized corrosion, it shows the visible signs of being affected prior which becoming structurally compromised. Therefore, before this type of corrosion happen which can completely ruins the asset, it need to have a long term maintenance.

The example of generalized corrosion is uniform corrosion. For localized corrosion, it is a corrosion that affect a specific location on a metal surface. It usually occurs in areas that is not plainly visible. It is difficult to detect the corrosion happens. The result is commonly failed or improperly applied coating. Examples of localized corrosion are pitting corrosion, crevice corrosion, filiform corrosion, intergranular corrosion, galvanic corrosion, stress corrosion cracking (SCC) and erosion corrosion.

2.2.1 Uniform Corrosion

Uniform corrosion is where the corrosion is attack over the entire exposed metal surface. It also the common type of corrosion and can happen over the large surface areas of material. This type of corrosion is also easily to predict and measure so it is not the most serious form of corrosion. It also refers to the corrosion that happen approximately the same rate over the exposed metal surface. It happens when the cast irons and steel exposed to open atmosphere, soils and natural waters which lead to the rusty appearance. In this situation, the cast irons and steels corrode uniformly.

For this type of corrosion, it is easy to measure and predict where it is rare in making the disastrous failures. There's several ways to prevent the uniform corrosion such as use the thicker material coatings such as plating, galvanizing or anodizing. Besides, se the corrosion inhibitors or modifying the environment can avoid the uniform

corrosion happen. Figure 2.3 shows the uniform corrosion on competitor's cast iron pump.



Figure 2.3 Uniform Corrosion on Competitor's cast iron pump

2.2.2 Pitting Corrosion

Pitting corrosion is the localized corrosion of a metal surface confined to a point or small area that takes the form of cavities. Pitting corrosion is one of the most damaging the forms of corrosion. Pitting corrosion is the most destructive type of corrosion. This is because it hard to predict, characterize and detect. It is a localized form of corrosion where it forms a small corrosion cell in the surrounding surface. It will grows into a cavity or hole which can forms variety of different shapes.

This type of corrosion can caused local break or damage to the metal. In liquids that containing chlorides, pitting corrosion can be seen on stainless steel and aluminium. It also has tendency to appear small and concentrated on the surface of metal where the metal is in fact, large and widespread beneath the surface. Figure 2.4 shows the pitting corrosion on stainless steel stator housing operating in seawater.



Figure 2.4 Pitting corrosion on stainless steel stator housing operating in seawater

2.2.3 Crevice Corrosion

Crevice corrosion is a localized form of corrosion. It also known as contact corrosion. It is similar with the pitting corrosion. It can be formed between two joining surfaces, for example, two metals or a metal and non-metallic material. It always happened in shielded areas where the oxygen is restricted such as bolt heads, under washes, etc. it can caused damage where it is close to joining the surfaces and confined to one metal at localized area. It also occurs under the gaskets, washers, clamps or even between a metal and barnacles in the case of permanently and frequently submerged assets. This is because the surfaces are partially shielded from the exposure to the outside environment by the materials adjacent to them. It is also difficult to detect and to defence against. It always happen during the building phase where instances in which it might occur are engineered out. Figure 2.5 shows the crevice corrosion on stainless steel nut exposed to seawater.



Figure 2.5 Crevice corrosion on stainless steel nut exposed to seawater

2.2.4 Filiform Corrosion

Filiform corrosion is a special form of corrosion that occurs under some thin coatings in the form of randomly distributed threadlike filaments. It also known as underfilm corrosion or filamentary corrosion. It occurs when penetrates of moisture have a protective barrier and settles between the barrier and the surface of metal. The barrier could be the metal plating, protective coating and other measurement that meant to provide the added protection for the surface of metals. The mechanism for this type of corrosion is allowed the oxygen and water to migrate. It also contains the highest concentrations at the back of the head in dissolved oxygen. This happened when the oxygen is reduced in the tail region, the metal ion dissolution and formation where it proceeds to the head. It also has a tendency of taking place in conditions with a high level of humidity.

Filiform corrosion also have been associated from the nitrates, carbonates, sulfates and condensates which contain halides. It can occurred in places where the conditions is slightly above the room temperature and the humidity level is at 75%. There is a thread-like filament appearance which the corrosion happen that dorms under the coating. Figure 2.6 shows the filiform corrosion.



Figure 2.6 Filiform Corrosion

2.2.5 Intergranular Corrosion

Intergranular corrosion is happened when the grain boundaries collide inside a metal. It always attacked immediately to grain boundaries while the bulk of grains are

remains unaffected. It is usually related to segregation of specific elements of the compound in the boundary. It is usually associated with chemical segregation effects where the impurities have a tendency to be enriched at grain boundaries or specific phase precipitated on the grain boundaries. The precipitation also can produce the zones that reduced corrosion resistance in the immediate vicinity.

This corrosion can happen when the temperature is between 500 and 800 °C. Chromium will react with carbon at grain boundaries at this temperature and form carbides. Chromium-rich grain boundary precipitates leads to a local depletion of CR is immediately adjacent to these precipitates where these areas leaving the vulnerable to corrosive attack in certain electrolyte. Reheating a welded component also a common cause of this type of corrosion during multi-pass welding. Figure 2.7 shows the intergranular corrosion between grain boundaries in metal.

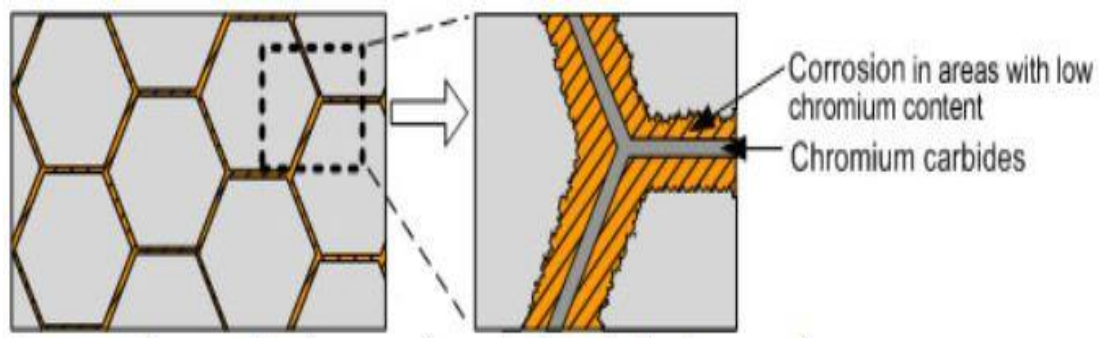


Figure 2.7 Intergranular corrosion between grain boundaries in metal

2.2.6 Stress Corrosion Cracking (SCC)

Stress corrosion cracking (SCC) is interpreted to take place due to specific combinations of susceptible materials in suitable corrosion environments under adequate stress, specifically under constant stress. Otherwise, stress corrosion cracking also the crack formation from combination of tensile stress and corrosive environment at elevated temperature. During manufacturing process, it can cause residual stress imparted such as from cold forming, machining, grinding, etc.

The effect of SCC on material is falls between the dry cracking and the fatigue of the material. It occur when the temperature below +60°C. It always occurred in specific alloy-environment-stress combination. Most of the surface is remains unattacked where

the fine cracks is penetrating into the material. The cracks have intergranular or transgranular morphology in the microstructure. It also has brittle appearance in macroscopic. Corrosion that based on exfoliation is the further form of intergranular corrosion which it is in high strength aluminium of alloys. The damage often initiates at end grains encountered in machined edges, holes or grooves and can subsequently progress through an entire section. Figure 2.8 shows the austenitic stainless steel subject to stress corrosion cracking.



Figure 2.8 Austenitic stainless steel subject to stress corrosion cracking

2.2.7 Galvanic Corrosion

Galvanic corrosion occurs in the presence of electrolyte when dissimilar metals are in contact with one another. The conditions that will provide galvanic corrosion happened are the temperature and surface of the metal for example, in saltwater environment, the copper is in contact with steel. To reduce the risk of galvanic corrosion, the metals need to be suitable together.

Galvanic corrosion can occur when it have two electrochemically which are different metals where it close to one another and submerged in an electrolyte liquid. When this condition occurred, it can create a galvanic cell where the cells can effects the corroding one metal at the expense of others. When the galvanic is formed, one of the metals become the anode and corrodes faster where can be done by itself while the other becomes the cathode and corrodes slower. Figure 2.9 shows the galvanic corrosion.



Figure 2.9 Galvanic Corrosion

2.2.8 Erosion Corrosion

For erosion corrosion, it is a combination of electrochemical corrosion where it related to the high speed of fluid. The pits formed when it usually have the bright surface free from corroded materials. It always attacked when localized to areas with turbulent flow and are provided by solid particles and gas bubbles. The causes of erosion corrosion which is the effect of flow or the velocity of a fluid together with the active corrosion of the fluid that can causes the accelerated loss of metal.

Erosion corrosion usually found at the high flow rated around tube blockages, tube inlet ends or in pump impellers. The prevent from erosion corrosion are control the fluid of velocity, using more resistant materials which is stainless steel, carbon steel and nickel aluminium bronze and using corrosion inhibitors or cathodic protection to reduce the erosion corrosion. The difference between erosion corrosion and flow accelerated corrosion is cavitation corrosion is a special form of erosion corrosion. That is can cause by water bubbles produced by a high speed impeller which then collapse and can cause pits on the mental surface on it. Figure 2.10 shows the erosion corrosion on impeller.



Figure 2.10 Erosion corrosion on impeller

2.3 Corrosion Treatment Technique

Corrosion has different methods to prevent it happen which are turn to non-corrosive metals such as aluminium and stainless steel. Keep the area around the metal surface dry. Make sure underground piping is laid in a layer of backfill such as limestone. And ensure that any electrical component are cleaned regularly

In industry, there are several treatments that can be used to prevent corrosion which are coating, cathodic protection and inhibitor that has many types of inhibitor. For inhibitor, it is explained further in 2.4.

2.3.1 Coating

Coating is to cover the object from corrosion. The purpose for using the coating is to improve the surface properties of bulk materials where it referred as a substrate. From this treatment, it can improve the appearance, adhesion, wear resistance, scratch resistance, corrosion resistance, etc. It can be tested and measured for proper opacity and thickness of film by using a Drawdown card. The coating that always used in industry is powder coating.

Powder coating is a coating where it applied as a dry powder and it is free-flowing. The difference between the powder coating and conventional liquid paint is the powder coating does not require solvent where it keeps the binder and filler parts in the liquid suspension form. The powder may be a thermoset polymer or thermoplastic. It is used to

create hard finish that is tougher than conventional paint. Powder coating are also mainly used for aluminium extrusions, automobile, coating of metals such as “whiteware” and motorcycle parts.

There are several advantages of powder coating. One of the advantages of powder coating is can produce much thicker coatings without running or sagging. Besides that, it also produces less hazardous waste for the production lines. Powder coating emit zero for volatile organic compound (VOC). It also can be recycled when it is overspray. It also has possibility to achieve nearly 100% use of the coating. Figure 2.11 shows the pipe with coating.

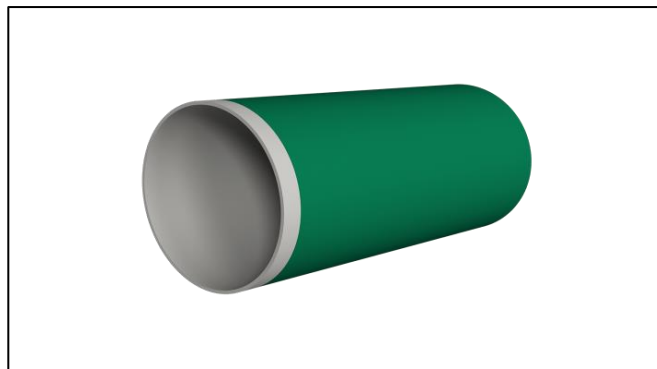


Figure 2.11 Pipe with coating

2.3.2 Cathodic Protection

Cathodic protection is an electrochemical process which is oxidation process in galvanic cell. In the galvanic cell, the concentrated is at anode while the corrosion is at the cathode in the same cell. It allows carbon steel which has little natural corrosion resistance to be used in many corrosive environments such as seawater, acid soils, etc. It can prevent corrosion instantly when it is properly designed and maintained. Sir Humphrey Davy is the first person who suggested used cathodic protection for controlling the corrosion on British naval ships. In 1930s, it has been used on Gulf Coast of the United States where it was used to prevent the corrosion of pipelines on carrying the high pressure natural gas and petroleum product. All modern pipelines are used both protection which are coating and cathodic protection where it can prevent the corrosion at gaps. Figure 2.12 shows the cathodic protection.

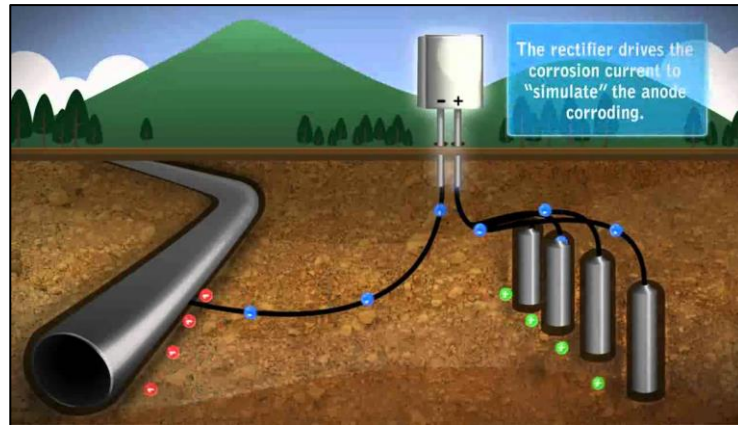


Figure 2.12 Cathodic Protection

2.4 Corrosion Inhibitor

A corrosion inhibitor is a chemical compound which added to industrial wastewater in order to reduce the rate of corrosion. It also a substances or mixtures that in low concentration and in aggressive environment inhibit where it can minimize and prevent the corrosion happen. It also can slows the attack of acid corrosion towards tubing, drill pipe and any other metals that contact with acid during treatment (Abdollahi *et al.*, 2012). The mechanism of the inhibitor is in several conditions which is the inhibitor is chemically adsorbed or known as chemisorption on the metal surface (Imran *et al.*, 2016). It also forms a protective thin film with effect of inhibitor or combination of the inhibitor ions and metallic surface.

Other than that, it also leads a film formation which through the protection of oxide of the metal base. It also reacts with potential corrosive component present in aqueous media and become a complex product (Camila *et al.*, 2014). There are several types of inhibitor that available in industries which are volatile, passivating (anodic), precipitation, cathodic, organic, inorganic and mixed. Figure 2.13 shows the process of corrosion inhibitor.

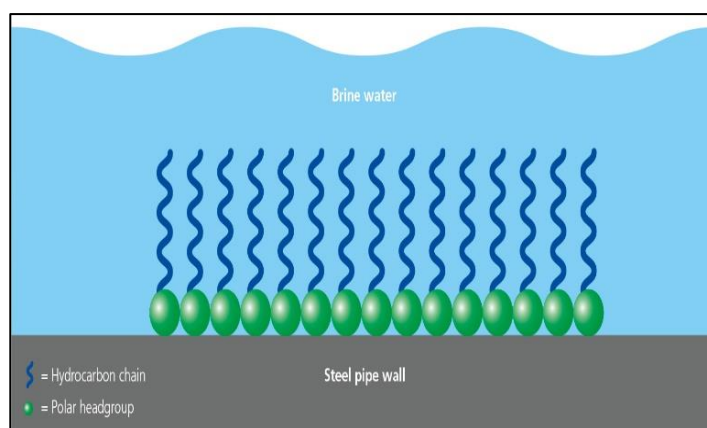


Figure 2.12 Corrosion inhibitor process

2.4.1 Volatile Inhibitor

Volatile inhibitor is known as vapour phase inhibitor. In vapour environment, corrosion is always occur so that it is useful to use the corrosion inhibitor into the system. It is good protection for metal surfaces where it can prevent the corrosion and rust for many years. It also a chemical that directly used on the metals which need to protect from rust. The adsorption of inhibitor will occur when the vapor contact the surface of metal. The moisture then hydrolyses it, hence protective ions may be released. The inhibition of ferrous metal is include the species such as nitrites and amines.

There are three types of volatile corrosion inhibitor which are VCI Foam emitters, VCI Films and bags and VCI papers. For VCI emitter, it used inside a package within the enclosed space to prevent corrosion on metal. It is effective because it has invisible layer of VCI protection where it can keeps the metal safe from corrosive that effects of salt, moisture, oxygen, dirt and other contaminants in environment.

For the VCI films and bags, it used for the barrier packaging with more effective which are the corrosion protection more clean, safe and easy packaging of machinery, metal parts and equipment. Lastly, VCI papers is for protect the ferrous metal such as cast iron and steel from rust. Figure 2.13 shows the process of volatile inhibitor.

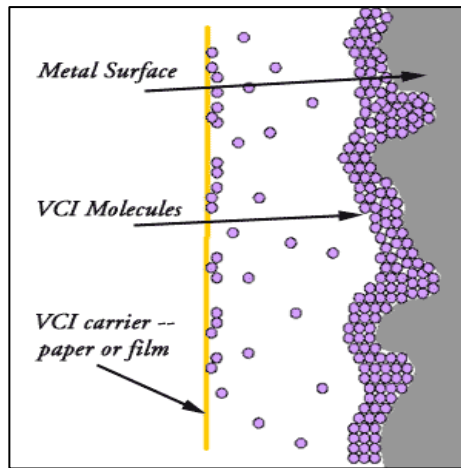


Figure 2.13 Process of Volatile Inhibitor

2.4.2 Passivating (Anodic) Inhibitor

Passivating inhibitor is called as anodic inhibitor. There is less current flow because of the anodic curve of polarization shift. There are two categories in anodic inhibitor which is oxidizing and non-oxidizing anions. In the absence of oxygen, oxidizing anions has the ability to passivate the metal. The type of oxidizing anions are nitrate, nitrite and chromate. Typical non-oxidizing anions are tungstate, molybdate and phosphate which need oxygen to perform passivation. Passivating inhibitor is the one inhibitor that used the most in industry and have higher efficiency compared to others inhibitor.

However, the concentration of the inhibitor must be managed well above minimum or critical concentration to maintain the sufficient passivation of the metal, thus need to provide sufficient inhibition. It suffer from localized corrosion if the concentration of inhibitor is below the minimum value. For this inhibitor, it will react with metallic ions to produce on the anode and formed insoluble hydroxides (Camila *et al.*, 2014). Figure 2.14 shows the illustration of the effect of anodic inorganic and action of mechanism.

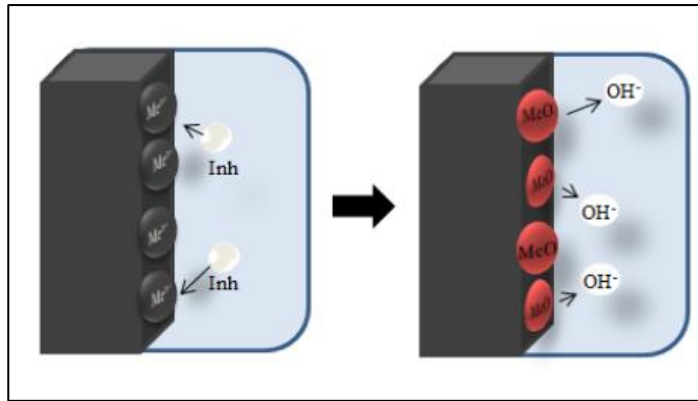


Figure 2.14 Illustration of effect of anodic inorganic and action of mechanism

2.4.3 Precipitation Inhibitor

This type of inhibitor is often film-forming where it is instance silicates and phosphates. They usually are blocking the anodic and cathodic sites. It formed protective barrier when they precipitate on the metal surface. Hard water is rich in calcium and magnesium. For example, when the pH is higher at the cathode, they produce a protection layer on the metal. There are two types of film forming that can be distinguished by two classes. The first case is it works by slowing down the corrosion without stopping it completely. The second case is they attack completely. However, for this inhibitor efficiency, it depends on the saturation index and pH value. The saturation index can be determined by the temperature and water composition. Figure 2.15 shows the process of precipitation inhibitor.

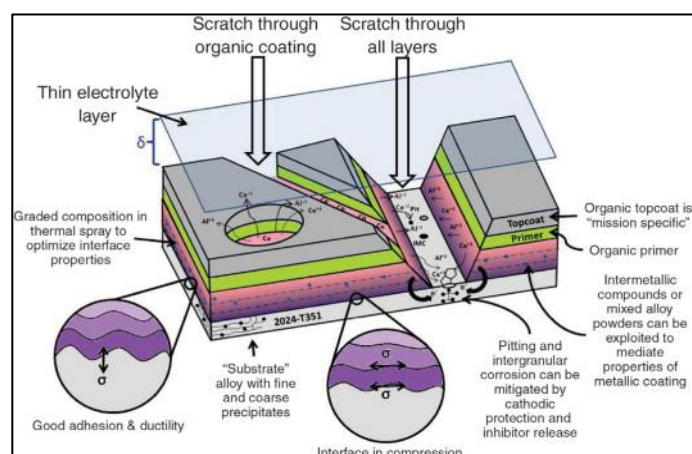


Figure 2.15 Process of Precipitation Inhibitor

2.4.4 Cathodic Inhibitor

Revie *et al* (2008) reported that cathodic inhibitor can reduce the reaction of cathodic. The name of process that happened is oxygen reduction near neutral environments and hydrogen evolution in acid solutions. It can lower the rate of diffusion and increase the surface impedance when the precipitate is on cathodic sites. It also can minimize the hydrogen ions release due to phenomena which can difficult the hydrogen discharge that called overvoltage. There are three mechanisms that take action for this inhibitor which are cathodic poisons, cathodic precipitates and oxygen scavenger.

Cathodic poisons is the reduction process that suppressed by the impeding the discharge and hydrogen recombination. In this case, it also may increase the tendency of metal to be susceptible to hydrogen induced cracking. In this process, it also may absorb the hydrogen where it can keep hydrogen in atomic form. There are two types of cathodic poisons which are antimony and arsenic. For cathodic precipitates, it can form a protective layer which acts as barrier on metal. Cathodic precipitates are compounds that precipitates as oxides which are magnesium and calcium. Oxygen scavenger is to reduce the corrosion by removal of oxygen in the system.

It formed a product when the compounds of oxygen scavenger react with oxygen in the system. Cathodic inhibitor is more independent about concentration and they are more secure than anodic inhibitor (Camila *et al.*, 2014). Figure 2.16 shows the mechanism of cathodic inhibitor.

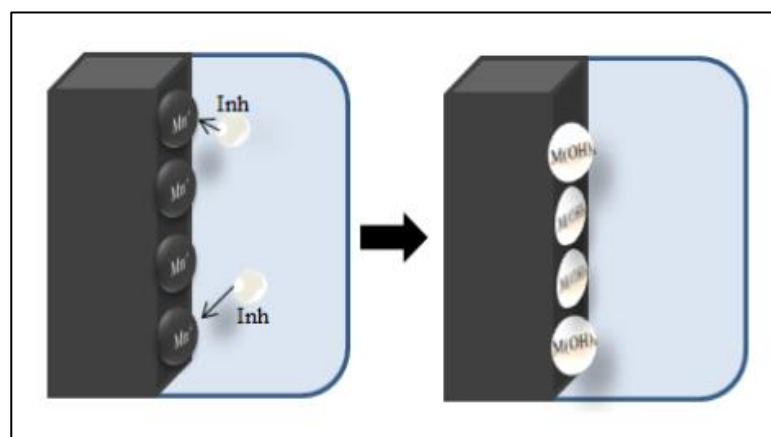


Figure 2.16 Illustration shown the mechanism of cathodic inhibitors

2.4.5 Organic Inhibitor

Organic inhibitor is film forming in nature where they form a layer on the surface on metal which called hydrophobic to prevent dissolution of metal. The efficiency of inhibitor is depends on the molecular structure of inhibitor itself, their affinity with metal as well as the chemical composition of metal. They are classified into two categories which are organic anions and cations. The types of organic anions are phosphonates and sulphonates. Amines groups and chemicals with active groups like aromatic and aliphatic are fall into the cations category. It is in the liquid or wax-like form for this type of inhibitor.

Organic inhibitor also can build up hydrophobic film that protect the adsorbed molecules on the surface of metal where it provide the barrier to dissolution of the metal. These inhibitor efficiency depends on the structure of chemical like the size of the molecule. It is related to the presence of polar functional groups with N, S or O atoms in molecule, pi electrons and heterocyclic which have hydrophobic or hydrophilic parts ionisable. The establishment of adsorption process is the polar function that regarded as the reaction center. There are several plant has been used as organic inhibitor which are aloe vera (Abiola *et al.*, 2010), Mollugo cerviana plant (Arockiasamy *et al.*, 2014), Tagetes erecta plant (Mourya *et al.*, 2014), Sida acuta plant (Umoren *et al.*, 2016), Musa Paradisa peel (Ji *et al.*, 2015) and etc. Figure 2.17 shows the mechanism of organic inhibitor.

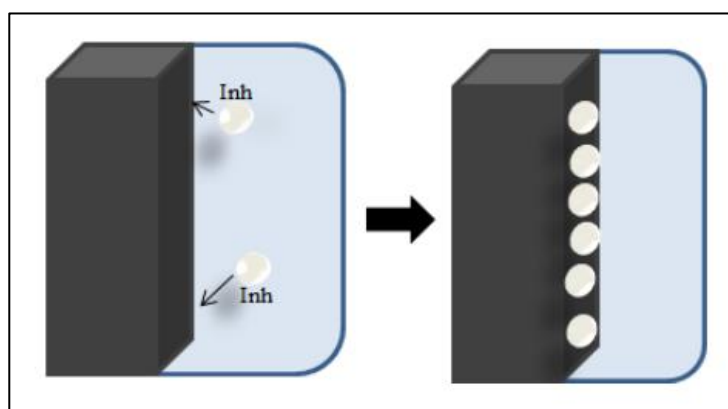


Figure 2.17 Illustration of mechanism of Organic Inhibitor

2.4.6 Inorganic Inhibitor

There are several common used inhibitors which are zinc phosphate, modified zinc phosphate, complex phosphosilicate, modified borates and complex borosilicates.

Crystalline salts is the common used for inorganic inhibitors. The sodium chromate and molybdate are also the type of this inhibitor. The negative anions that carry is to reduce the corrosion where it is the only active groups of these compounds. Figure 2.18 shows the process of inorganic inhibitor

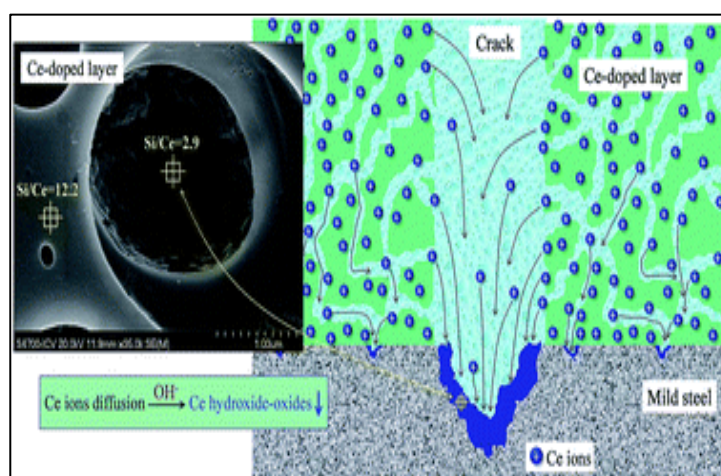


Figure 2.18 Process of inorganic inhibitor

2.4.7 Mixed Inhibitor

Mixed inhibitor is used more than one inhibitor where they carry different character. This is because it is rarely used as a single compound only. There are some factors that need to use more than one inhibitor. The first factor is can get the advantages when the anodic and cathodic inhibitor are combined together where can optimised the best performance. The second factor is by adding the halide ions, it can improve the action of organic inhibitor in acid solutions. Last factor is where a single inhibitor just can inhibit a few numbers of metals. However, sometimes the inhibitive action may cause the jeopardizing effects to other metal when the environment is involved with multi-metal system. Figure 2.19 shows the mixed inhibitor process.

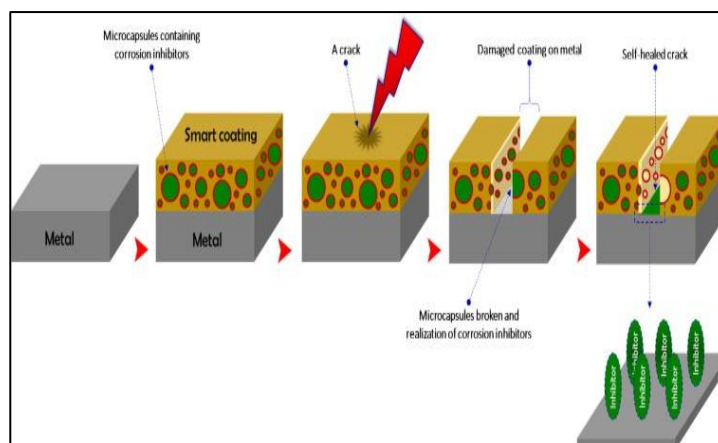


Figure 2.19 Mixed inhibitor process

2.5 Adsorption Process

Adsorption is the attachment of substance on the surface of a solid or liquid. (Abeng *et al.*, 2017). Adsorption behaviour can happen when the metal surface for adsorbate is known. It happens when it has interaction between the metal surface and inhibitor molecules which can be provided from adsorption isotherm. The efficiency of corrosion inhibitor depends on the adsorption ability on the metal surface (Fouda *et al.*, 2015). The adsorption of organic compound is described from the two main types of interaction which are chemisorption and physical adsorption (Physi-sorption).

For physi-sorption, the atoms or molecules are attached to surfaces by van der Waals interaction between the adsorbent and adsorbate where the van der Waals interaction has a long range but weaker forces. The attachment and separation can happen during this process. In chemisorption, the atoms or molecules are stuck together to the surface by forming the covalent bond and tend to find sites which can maximize their coordination number with the adsorbent (Abeng *et al.*, 2017). It is also influenced by the change of the nature of the metal, chemical structure of inhibitor, electrolyte type, pH and temperature. In this isotherm, it is very important in order to determine the mechanism of organic electrochemical reaction (Alwan, 2013).

For different concentration of inhibitor, the degree of surface coverage (θ) was evaluated by $IE/100$. The data can be applied through various isotherms which are Langmuir, Frumkin, Flory-Huggins and Temkin isotherms (Prabhu *et al.*, 2013). It also

an ideal isotherm for chemical and physical adsorption (Chaudhari *et al.*, 2016). Prabhu *et al* (2013) also reported that Langmuir adsorption isotherm was the best data fit and it represented by using the following equation:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad 2.1$$

Where the K is the adsorption or desorption of equilibrium constant, C is the concentration of corrosion inhibitor and θ is the surface coverage. The formula of θ is:

$$\theta = \frac{IE}{100} \quad 2.2$$

From the calculation above, the Langmuir graph can be plot of C/ θ versus C and gave a straight line with the intercept of 1/K.

2.6 Henna Leaves as Inhibitor

The scientific name of henna leaves is *Lawsonia Inermis* and it belongs to the family Lythraceae. It has several names in different language, for example, they called alhenna in English, henna in Arabic, mehndi in Hindi, tien kao in Thailand, etc. sometimes, the species is clarified as *La Sonia alba* Lam or *Lawsonia reba* and it also has a fragrant white or rose-red flowers. It is a small tress which has the height between 2 to 6m. It can grow with minimum temperature stay above 11°C. it can tolerates with extreme heat and long droughts. It also grows wild near the desert oasis and also in semiarid regions. It has the annual precipitation of 0.2 to 0.4 m and a soil pH of 4.3 to 8.0 where it thrives in alluvial soils. The leaves are in greenish brown to dull green in colour, small and sub-sessile where it have either a obtuse, acute apex or glabrous with abtapering base.

Henna plant is known as healing attributes but now it is a subject of intense scientific study. It also used for treatments purpose such as wounds, ulcer, ronchintis, cough, lumbago, leucoderma, boils, anaemia, boils, falling of hair, fever, haemorrhages, scabies, greyness hair, dysentery, etc. it also known as cosmetic agent that used for stain hair, skin and nails (Kidanemariam *et al.*, 2013).

The leaf is known as hennotannic acid where it contains red-orange color component, lawsone (2-hydroxy-1, 4-napthoquinone)(Kidanemariam *et al.*, 2013). The

moisture and soil are affects the henna's Lawsone levels where hot, dry, and iron bearing soils can produce the henna with lower level of Lawsone. It also contains the tannin, resin, gallic acid, sterols and coumarins where the main components of henna extract is tanning and lawsone which called hydroxyl aromatic compound. The inhibitive action of tannin attributes to the formation of a passivating layer of tannates on the metal surface. The main constituent of henna extract is Lawsone. The structure of Lawsone is shown in Figure 2.20 where it contains benzene unit, p-benzoquinone unit and phenolic group. Figure 2.21 shows the picture of henna trees.

Lawsone is the chief constituent responsible for the properties of dying of the plant where the dried powdered of henna leaves is contained about 0.5 to 1.5% Lawsone. It can forms the color which are fast orange, red and brown dyes. The Lawsone molecules also a ligand which can chelate with various metal cations where it formed the complex compound. Thus, the formation of the insoluble complex compound from the combination of the metal cations and molecules of Lawsone is adsorbed on the metal surface (Abdollahi *et al.*, 2012). From the GC-MS analysis, there are at least twenty eight of components is presence in this leaves. However, just nine compounds that are identified. The constituent of the essential oil of leaves is as shown in table 2.1:

Table 2.1 Chemical Composition of essential oil of *L.inermis* leaves

Retention Time (min)	Compound	Composition (%)
7.56	Linalool ^M	4.23
10.48	A-terpineol ^M	8.36
11.42	Etherphenylviny ^A	6.72
15.32	1,3-indandione ^A	6.62
15.91	Eugenol ^A	17.61
21.04	Cis-hexahydro-8a-methyl,8- [2H,8H]-naphthalenedione ^K	5.60
29.23	Oxirane-tetradecyl ^E	6.20
32.53	Hexadecanoic acid ^F	15.07
35.99	Phytol ^D	10.17

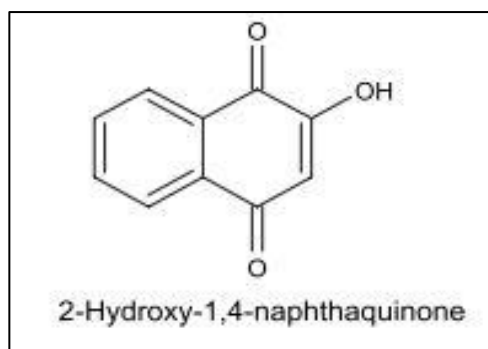


Figure 2.20 Lawsone Structure



Figure 2.21 Henna trees

Lawsone molecule is a ligand that can chelate with various metal cations that formed complex compound. Thus, the formation of insoluble is complex compound where the combination of the metal cations and the molecules of Lawsone adsorbed on the metal surface. It is a probable interpretation of the observed inhibition action of Lawsone. Derealisation of the lone pair of electrons on hydroxyl group takes place resulting in the rearrangement of lawsone structure in acidic medium. In the presence of metal cations, it enhances the formation reaction such as rearrangement (Abdollahi & Shadizadeh, 2012).

Lawsone inermis is the chief constituent responsible for the dying properties of plant. For the dried powdered henna leaves, it contains about 1.5% of lawsone which traditionally used to produce color fast orange, red and brown dyes (Kidanemariam *et al.*, 2013).

There are few studies that have investigated about the henna leaves can be used as corrosion inhibition on a metals (Hamdy *et al.*, 2013). It also has anti-inflammatory, antipyretic and analgesic effect where in aggressive solution, it has inhibitory action on steel and aluminium (Rajendran *et al.*, 2009).

Ostovari *et al* (2009) had investigate about the corrosion inhibition of mild steel in 1 M HCl solution by henna extract. From this study, it shown that inhibition efficiency of mild steel increases with increase of henna extract concentration. When the HCl solution contained 0.2g/L, the inhibition efficiency is 59.26% where it is the lower efficiency compared to 1.2g/L which the inhibition efficiency is 92.59% at 25°C. At 40°C, the lowest efficiency is 36.34% when the henna leaves extract is 0.2g/L while the highest efficiency is 69.66% when the concentration of henna leaves extract is 1.2g/L. For the 50°C, the highest efficiency is 54.38% at 1.2g/L while the lowest efficiency is 20.17% at 0.2g/L. in this study, the highest temperature is 60°C. In this case, the lowest efficiency is 9.63% at 0.2g/L while the highest efficiency is 37.95% at 1.2g/L. From the result, when the temperature increases, the inhibition efficiency is decreases. At 40, 50 and 60°C, maximum inhibition efficiency of 69.66, 54.38 and 37.95% were obtained in 1 M HCl solution that contain 1.2 g/l of henna extract. At 25°C, it has the highest efficiency which is 92.59%. Based on the result, the rate of corrosion increase is more pronounced with the rise of temperature for uninhibited acid solution. Therefore, the presence of inhibitor leads to decrease of the rate of corrosion.

The second journal that can compare is from Chaudhari *et al* (2016) where in this research topic is henna leaves extract as green corrosion inhibitor for mild steel in acetic acid. Based on the result, the corrosion loss has been increased from 486.41 to 891.75 mg/dm³ in 1.0 to 2.0 M acetic acid solution. Therefore, the rate of corrosion will increases with the increase of the concentration of the acid. The rate of corrosion is directly proportional to the concentration of acid.

Figure 2.22 and 2.23 are the Langmuir adsorption isotherm for henna leaves extract in 0.5 M acetic acid and Langmuir adsorption isotherm plot for the adsorption of henna leaves extract in 1.0 M acetic acid solution at different temperature. It was plotted by using the equation of Langmuir. From the both graph, C / θ is directly proportional to

concentration of inhibitor. It shows that the inhibitor is a good adsorption of the corrosion process.

At different temperature, for 313 K, it has the highest reading of Langmuir adsorption where it shows at this temperature, the inhibitor is good at lower temperature. When the temperature increase, it leads to the increase in desorption of the adsorbed inhibitor molecule from the mild steel surface.

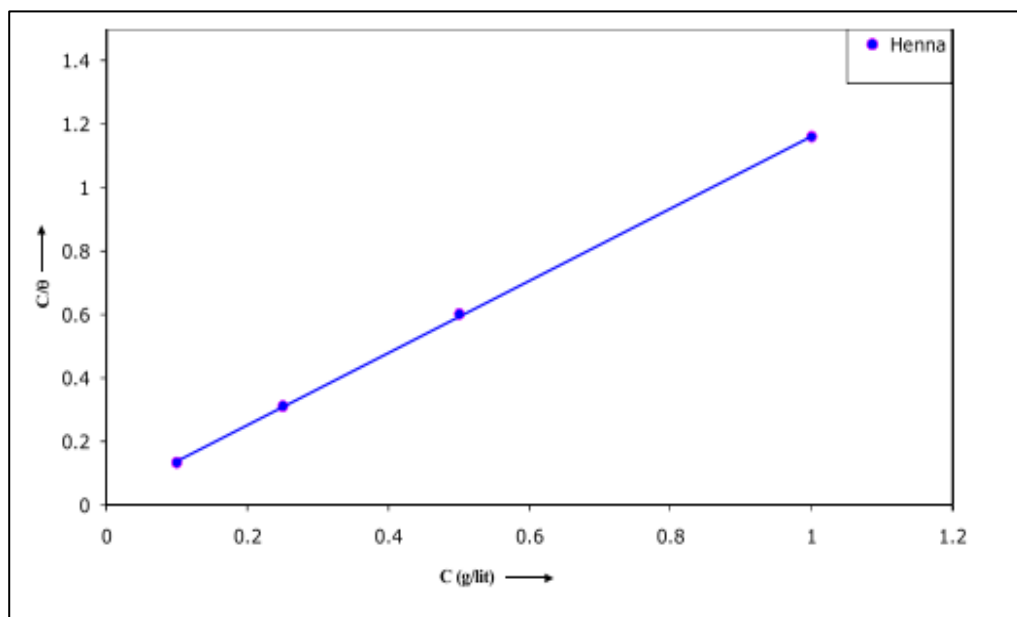


Figure 2.22 Langmuir adsorption isotherm for henna leaves extract in 0.5 M acetic acid

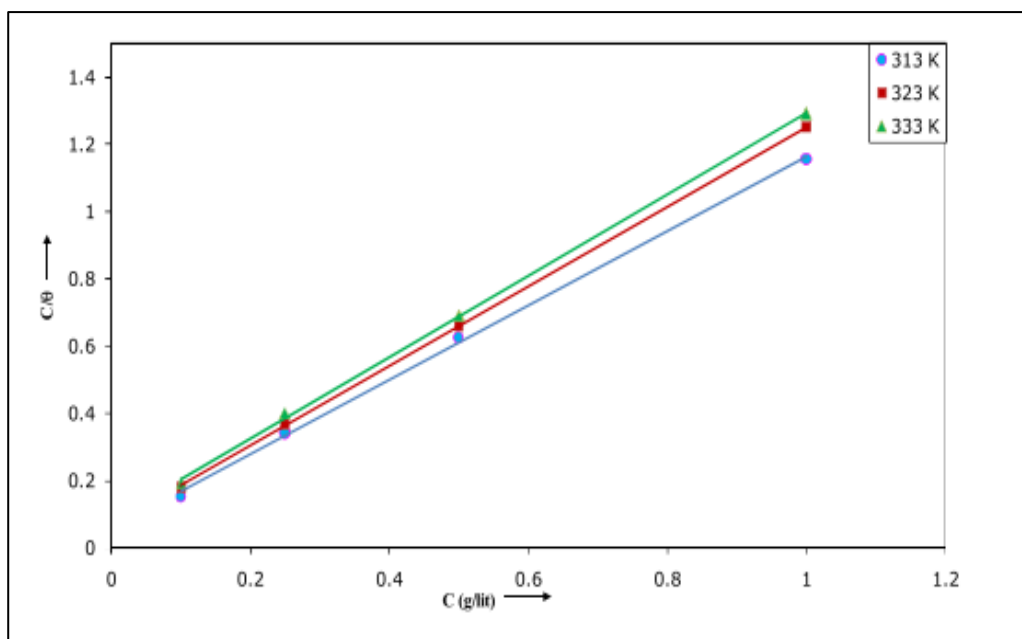


Figure 2.23 Langmuir adsorption isotherm plot for the adsorption of henna leaves extract in 1.0 M acetic acid solution at different temperature

Hamdy *et al* (2013) also had investigated the corrosion parameters obtained from the weight loss of steel in 1M HCl containing various concentration of henna extract at different temperature. The temperature that done in this study were 293K, 303K, 313K, 323K and 333K. the concentration of henna leaves extract that used in this study were 0mg/L, 100mg/L, 500mg/L, 1000mg/L, 2000mg/L and 3000mg/L. From the result that obtained, at 293K, when the concentration of henna leaves extract is 100mg/L, the inhibition efficiency is 36.21 while at the highest concentration which is 3000mg/L, the inhibition efficiency also the highest which is 88.42%. When the concentration is 100mg/L at 303K, the inhibition efficiency is 33.44% while at 3000mg/L, the inhibition efficiency is 85.32%. When the temperature is at 313K, the highest inhibition efficiency is 79.52% which the concentration is the highest. At 323K, the highest efficiency is 75.69%. Lastly, at 333K which is the highest temperature in this study, the highest inhibition efficiency is 67.73%. From the result, it shows that the higher the concentration of henna leaves extract, the higher the inhibition efficiency. For the temperature, when the temperature is lower, it shows that the inhibition efficiency is higher compared to the higher temperature.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter presents the methodology used to achieve the objectives of the study where it explained details about the procedure of the field of study and the analysis of methods. In section 3.2 provided the description of materials and equipment. The analytic method are explained in section 3.3 and experiment set up explained in section 3.4. Figure 3.1 shows the study framework for the whole experiment of study.

3.2 Materials and Method

3.2.1 Water Solution

The preparation of solution was about 1M HCl solutions where it prepared by dilution of 37% HCl (Merck) using distilled water. The volume of distilled water used was 86.2 ml and the remaining was filled up with 1M HCl in 1000 ml volumetric flask.

3.2.2 Henna Extract

Henna is known as *Lawsonia Inermis*. This type of plant can be found in hot climates of country such as Egypt, India, Africa and Morocco. It was collected from the person who has henna tree. The process of preparing henna was started by grinding the leaves and put in the boiled water for 2 hours. Figure 3.2 below shows the henna leaves. Figure 3.3 shows the henna leaves during grinding. Figure 3.4 shows the henna leaves was boiled for 2 hours.

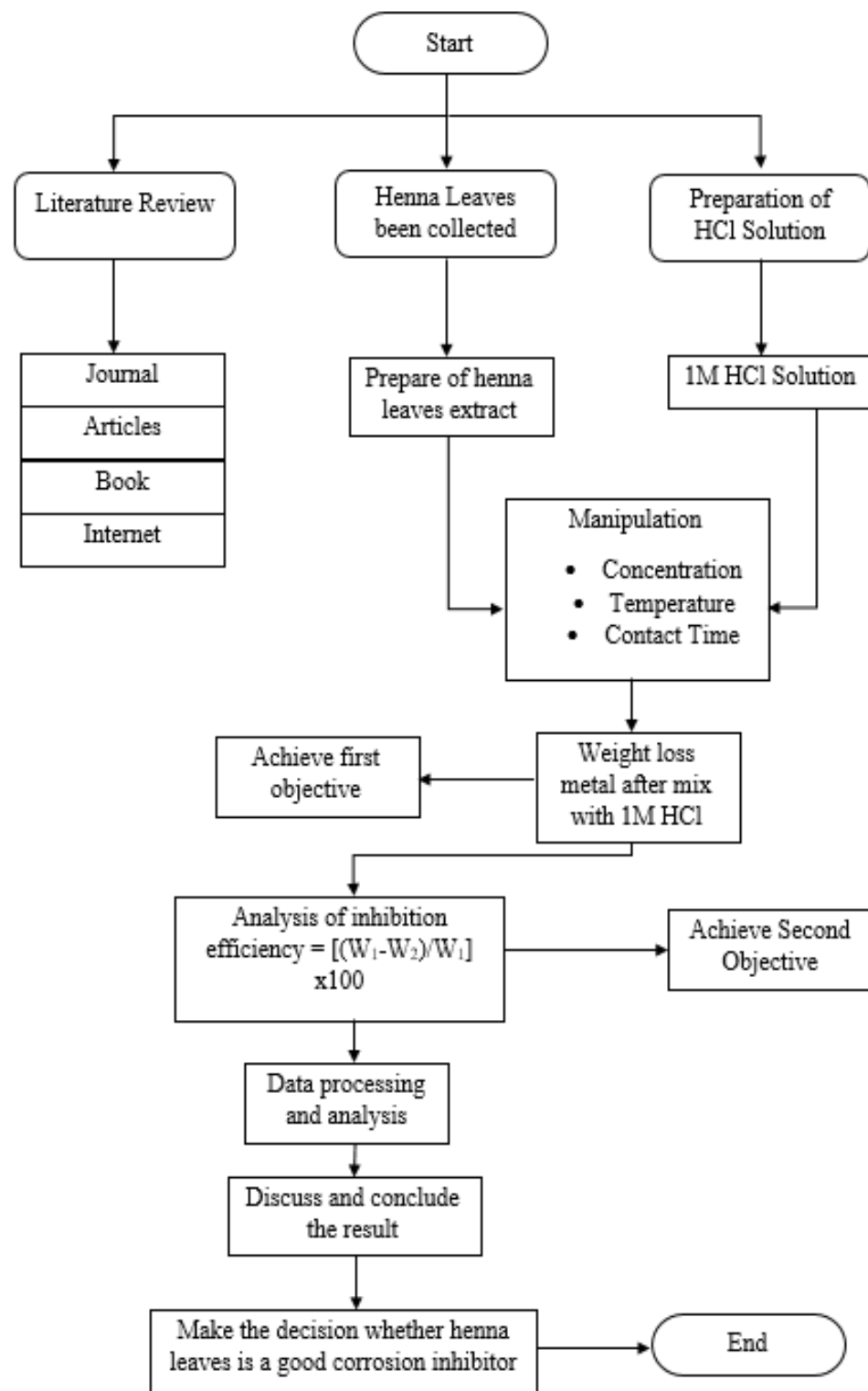


Figure 3.1 Study Framework of the Whole Experiment Study



Figure 3.2 Henna Leaves



Figure 3.3 Henna leaves during grinding process



Figure 3.4 Henna leaves during boiled process

3.2.3 Mild Steel Study

Materials that used during this study was the mild steel as the subject in this study. Every sample of different concentration of henna was provided 200mL of hydrochloric acid. The hydrochloric acid was prepared before conduct the experiment. Figure 3.5 shows the mild steel that used in this experiment.



Figure 3.5 Samples of Mild Steel

3.2.4 Equipments

In this study, the equipments that used were in table 3.1:

Table 3.1 Equipment

Equipments	Brand	Application
Kitchen's Mill	Blendtec	To crushed the leaves
500mL Beaker	BORO 3.3	To put the chemical and heat it up for henna leaves extract
Hotplate/Magnetic Stirrer	Hp-3000	To heat the solution
Filter	Eco	To remove any contamination of henna leaves
Thermostated Water Bath	Memmert	To put the chemical that need to heat up for days.
Measuring Cylinder	Brand TM	To measure the volume of the solution
Weighing Balance	Contech	To weigh the weight of henna leaves extract

Figure 3.6 shows the kitchen's mill that used to crush the henna leaves. Figure 3.7 shows the 500mL beaker to put the chemical and boiled the henna leaves extract. Figure 3.8 shows the hotplate to heat the solution. Figure 3.9 shows the filter to remove any contamination of henna leaves after boiled. Figure 3.10 shows the thermostated water bath to put the chemical which need to heat up for days. Figure 3.11 shows the measuring cylinder to measure the volume of solution. Figure 3.12 shows the weighing balance to weigh the weight of henna leaves extract.



Figure 3.6 Kitchen's Mill



Figure 3.7 500mL Beaker



Figure 3.8 Hotplate / Magnetic Stirrer



Figure 3.9 Filter



Figure 3.10 Thermostated Water Bath



Figure 3.11 Measuring Cylinder



Figure 3.12 Weighing Balance

3.2.5 Reactor Set Up

The preparation of henna leaves used the kitchen's mill to crush the leaves and boiled it. Then, HCL solution was prepared and put on the henna leaves. Then, the subject that used in this study was mild steel where the mild steel presented the metal in HCl solution. Therefore, from the mild steel, it identified the weight loss of metal, rate of corrosion and the efficiency of inhibitor.

3.3 Analytical Method

This experiment was observed through three parameters which were rate of corrosion, weight loss of metal and inhibition efficiency.

3.3.1 Weight Loss of Metal

The weight loss of method was determine whether the mild steel have been corroded or not where the mild steel was needed to be weighed and recorded after few days. This method has major advantage where it was simplicity and availability.

3.3.2 Rate of Corrosion

The rate of corrosion was determined from the weight loss measurements where it computed at various concentration of henna. The formula was shown in equation 3.1:

$$Cr = \frac{\Delta W}{At} \quad 3.1$$

Where:

Cr = Rate of Corrosion, $\text{g m}^{-2} \text{h}^{-1}$

ΔW = Weight Loss of Sample, g

A = Area of Exposure, m^2

t = Immersion Time, h

3.3.3 Efficiency of Inhibitor

From the weight loss, it calculated the inhibitor efficiency where can know whether the inhibitor chosen was a good corrosion inhibitor or not. The formula for inhibition efficiency was shown in equation 3.2:

$$IE = \left(\frac{W_1 - W_2}{W_1} \right) \times 100 \quad 3.2$$

Where:

IE = Inhibition efficiency, %

W_1 = weight loss of metal in absence of inhibitor, g

W_2 = weight loss of metal in presence of inhibitor, g

3.4 Adsorption Isotherm

Adsorption isotherm used to understand the mechanism of corrosion inhibition of metals and alloys. The Langmuir adsorption isotherm employed when the adsorption of henna leaves extract molecules was due to monolayer adsorption and ignored the

interaction between adsorbed molecules. The equation of Langmuir adsorption was as followed:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad 3.3$$

Where

K is adsorption equilibrium constant

C is concentration of inhibitor

$$\theta = IE/100$$

The Langmuir graph plotted is C/θ direct proportion with C.

3.5 Experiment Set Up

The henna solution and mild steel was put in a beaker of 500mL and HCl solution poured in it for 200mL. The experiment were conducted at room temperature for a total of 30 days. Five different concentration of henna extract were tested to determine the optimum dosage of henna extract. Henna leaves and HCl solutions were prepared where HCl solutions presented as industrial wastewater. Henna leaves was crushed and extracted in boil water for 2 hours. The solution was filtered to remove any contamination. Next, the test solution was put in the thermostated water bath with different temperature for 24hours. The mild steel was taken out and weighed. The step was repeated for different concentration of henna leaves.

To investigate the corrosion inhibition properties, the solid extract need to prepare the required concentration of henna. For the preparation of solution, 1 M HCl was prepared by dilution of 37% HCl by using distilled water. The range for concentration of henna extract was between 5 to 35 g/L. Figure 3.13 to 3.16 shows the experiment that done in the laboratory.



Figure 3.13 Henna leaves crushed

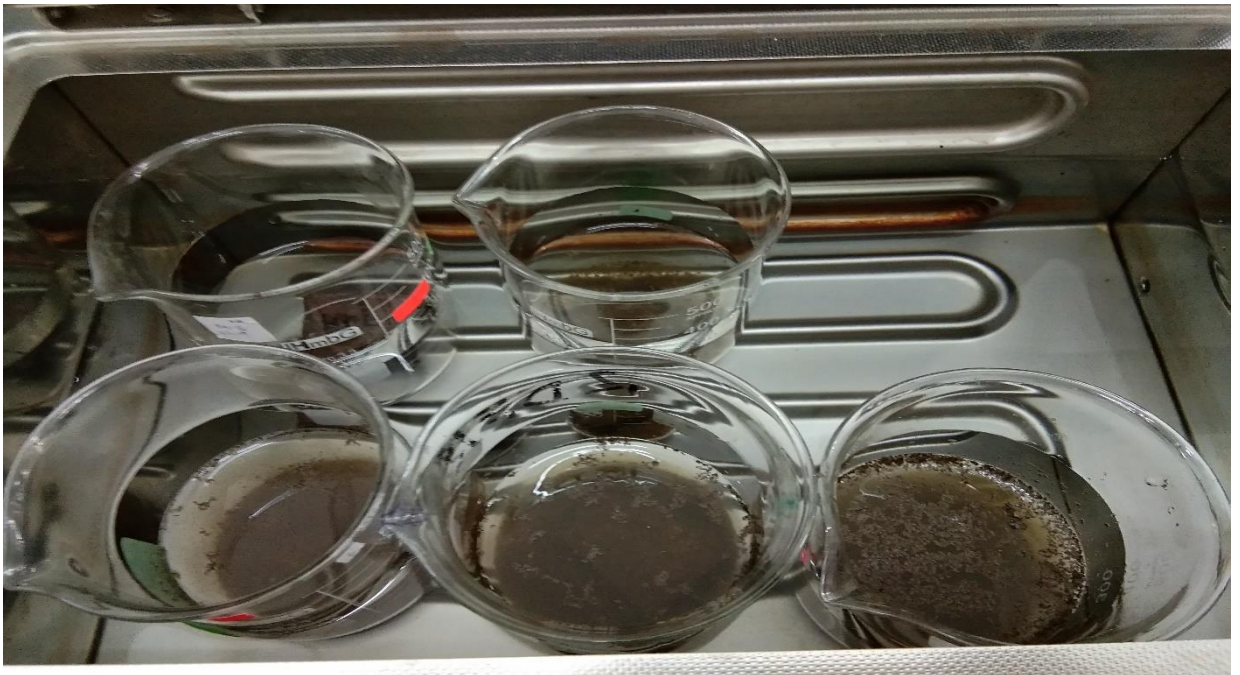


Figure 3.14 Process corrosion in thermostated water bath

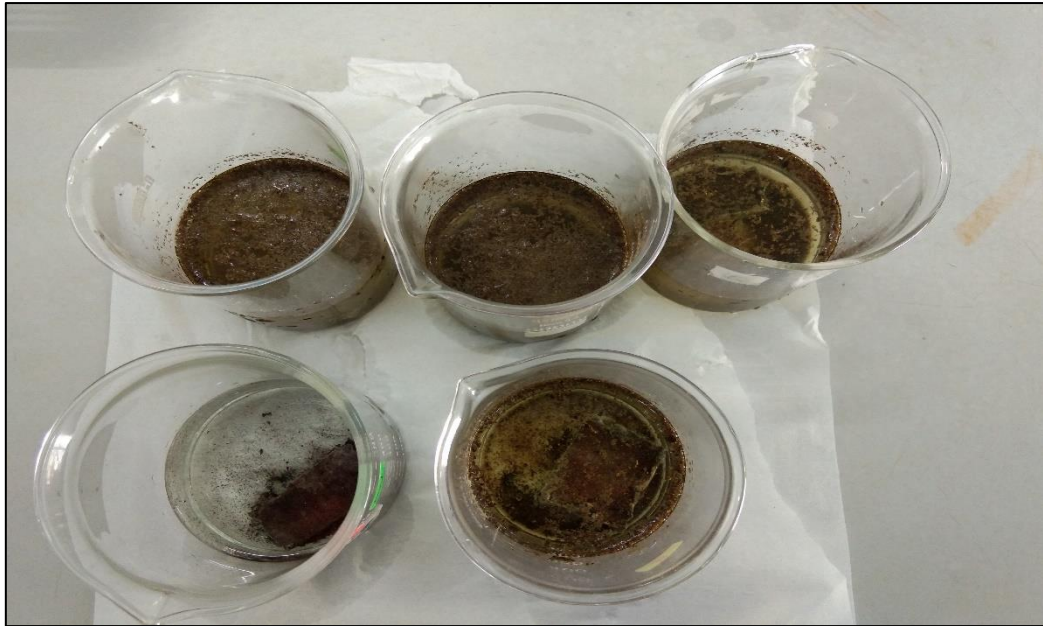


Figure 3.15 After 1 day in thermostated water bath



Figure 3.16 After 1 month at room temperature

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

In this chapter 4, it described about the results and discussion of the corrosion inhibition by henna leaves extract in industrial wastewater. This chapter discussed about the optimum concentration of henna leaves extract and compare the effect of contact time and temperature of inhibitor on mild steel.

4.2 Determination of Optimum Concentration of Inhibitor

The parameter of corrosion was obtained from conducting the weight loss measurement for mild steel in the absence and presence of different concentration of extraction of henna leaves in 1M HCl at room temperature were tabulated in Table 4.1. Table 4.1 shows that the corrosion rates and inhibition efficiency for the mild steel immersed in 1 M HCl for 30 days. The result shows the graph was unmanufactured where the rate of corrosion decreased as the concentration of henna leaves extract was at 5g/L. In this case, it was because of the higher adsorption level of active inhibitor molecules from the extract on the metal surface.

For the concentration 15 to 35 g/L, the corrosion rate almost constant. The inhibition efficiency was calculated based on the weight loss method. The inhibition efficiency was increased linearly with the concentration of henna leaves extract. When the inhibitor concentration increase, the number of molecules adsorbed over the mild steel also increase where it blocked the acid attack at active sites which can protect the metal surface from corrosion. It was apparent that the optimum dosage that can used was 35g/L. Figure 4.1 shows the corrosion parameters for mild steel in 1M HCl containing various concentration of henna leaves extract.

Table 4.1 Corrosion Parameters for Mild Steel in 1M HCl containing various concentration of henna leaves extract

Concentration of Inhibitor, (g/L)	Weight Loss, WL (g)	Rate of Corrosion, (g m ⁻² h ⁻¹)	Inhibition Efficiency, (%)
0	6.58	2.01	-
5	6.50	1.95	5.02
15	6.92	2.13	5.14
25	6.50	2.10	5.29
35	5.10	2.12	6.00

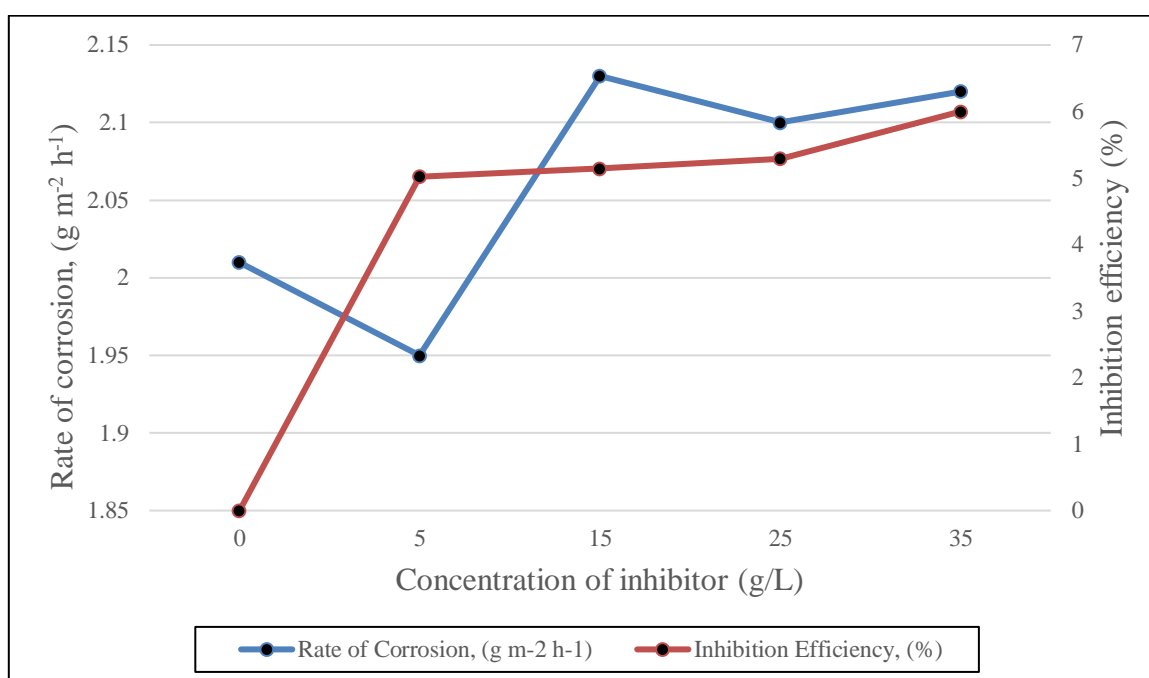


Figure 4.1 Corrosion parameters for mild steel in 1M HCl containing various concentration of henna leaves extract

4.3 Effect of Henna Leaves Extract at Different Temperature on Mild Steel

The optimum dosage of henna extract was 35g/L which had been achieved in the first objective. The temperature that used in this study was 25°C, 40°C, 50°C and 60°C. Based on the table 4.2 below, it shown that the higher the temperature, the inhibition efficiency was increased. When the temperature was 25°C, the inhibition efficiency was 1.84% while at 60°C, the inhibition efficiency was 6.29%. It was found that the lower the temperature, the inhibition efficiency also decrease. A possible explanation for these

results may be due to the metal surface have many change such as desorption and rapid etching of inhibitor where the inhibitor itself can undergo decomposition and rearrangement. Ostovari *et al* (2009) reported that when the temperature increase, the inhibition efficiency is decrease. When the temperature was 25°C, the inhibition efficiency was 92.59% while at 60°C, the inhibition efficiency was 37.95%.

Therefore, from the result obtained, it can see that the higher the temperature, the higher the inhibition efficiency of henna leaves extract. Figure 4.2 shows the effect of temperature on mild steel in 1M HCl.

Table 4.2 Corrosion Parameters for Mild Steel in 1M HCl containing 35g/L at various temperature

Temperature (°C)	Weight Loss, WL (g)	Rate of Corrosion, (g m⁻² h⁻¹)	Inhibition Efficiency, (%)
25	1.71	21.8	1.84
40	3.34	25.74	2.37
50	3.67	50.67	4.55
60	5.03	80.86	6.29

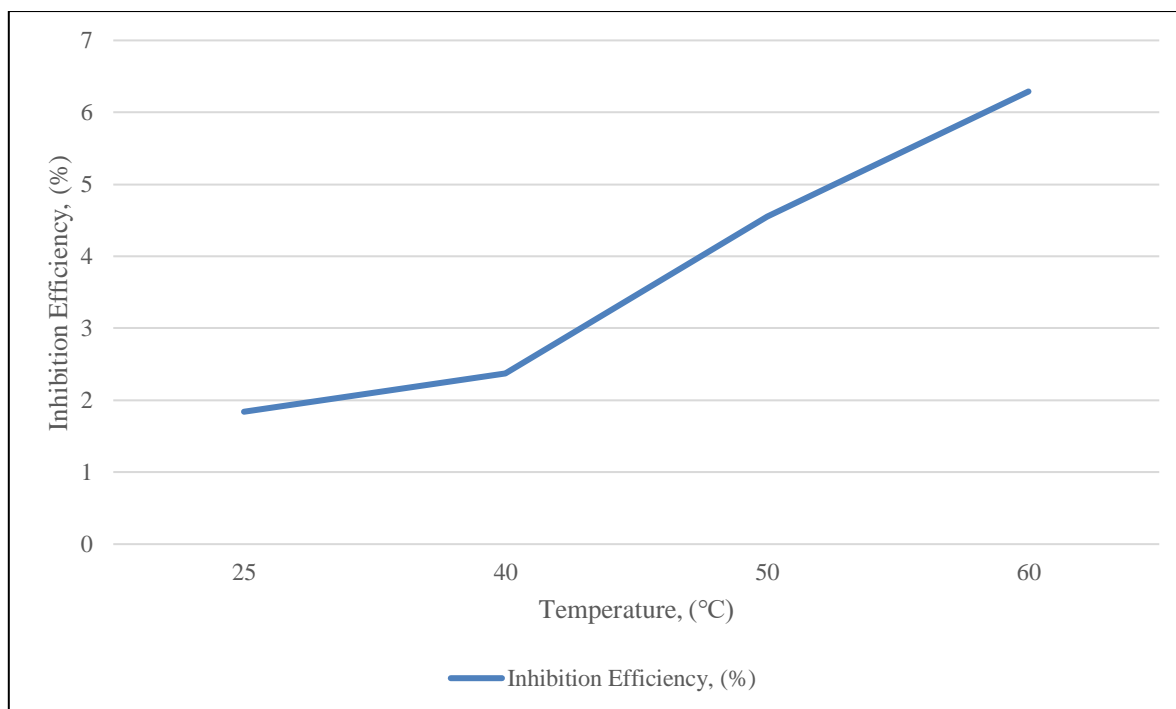


Figure 4.2 Corrosion parameters for mild steel in 1M HCl containing 35g/L at various temperature

4.4 Effect of Contact Time of Inhibitor on Mild Steel

The optimum concentration that used in this study after achieved the first objective was 35g/L. The contact time that taken for this study is 30 days where the reading was taken after 7 days. After 30 days, the reading of inhibition efficiency shows the increase of percentage reading. The result in table 4.3 shows that when the time taken was forth week, the inhibition efficiency shows the highest percentage which was 6%. It can be seen in figure 4.3, at week three and four, the inhibition efficiency was almost same. This findings shows that the inhibitor was good for the long term inhibitor in order to decrease the corrosion happen in industrial wastewater.

Table 4.3 Corrosion Parameters for Mild Steel in 1M HCl containing 35g/L of Contact Time

Week	Inhibition Efficiency, (%)
1	4.08
2	5.21
3	5.89
4	6.00

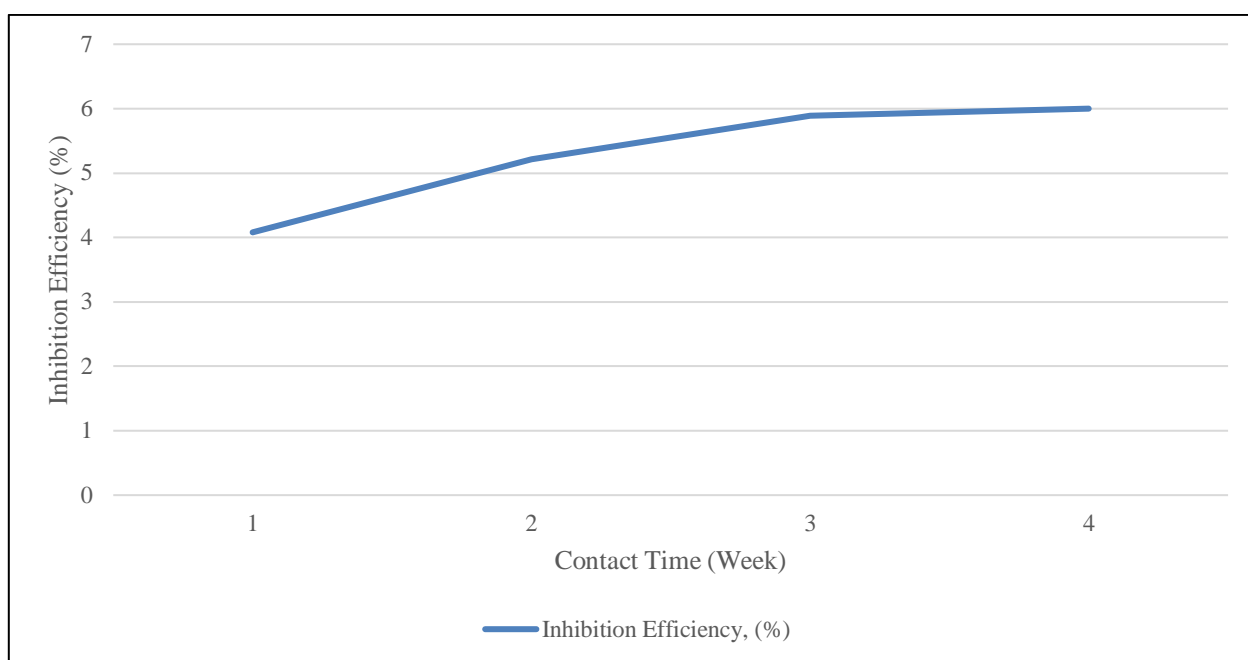


Figure 4.3 Corrosion parameters for mild steel in 1M HCl containing 35g/L of contact time

4.5 Adsorption Isotherms

The C/θ versus C at room temperature was plotted in Figure 4.4. All plots give straight lines with almost unit slope. By using weight loss method, the observed behaviour can be obtained. From the behaviour, it can be confirmed that the adsorption of henna leaves extract obeys Langmuir adsorption isotherm. Table 4.4 below shows the value of C/θ . From the graph, the Langmuir equation was $y=17.011x + 17.291$. It can be concluded that henna leaves were a good inhibitor for the adsorption process. It is shown that the graph was C/θ directly proportional to the C .

Table 4.4 Langmuir Isotherm for Adsorption of Henna Leaves Extract onto Mild Steel in 1M HCl

Concentration of Inhibitor, C (g/L)	$\frac{C}{\theta}$
0	-
5	99.60
15	291.83
25	472.59
35	583.33

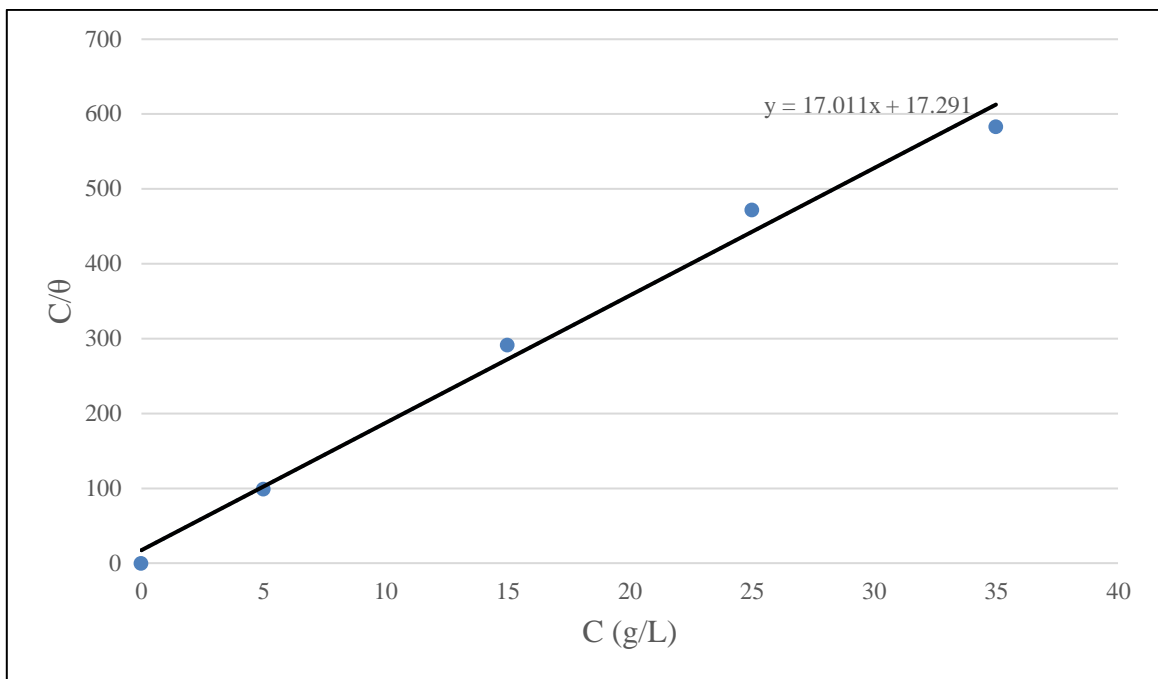


Figure 4.4 Langmuir isotherm for adsorption of Henna leaves extract onto mild steel in 1M HCl

CHAPTER 5

CONCLUSION

5.1 Introduction

Conclusion is a closure for the reader where it remind them about the contents of the study. In this chapter, it described the conclusion and recommendation in order to improve this study which discuss in section 5.2 and 5.3.

5.2 Conclusion

From the objective of this study which is to determine the optimum dosage of inhibitor based on the weight loss of mild steel and compare the effect of contact time and temperature of inhibitor on mild steel. From the result that obtained, it can conclude that:

- i. The optimum dosage of henna leaves extract is 35g/L.
- ii. At higher temperature which is at 60°C, the inhibition efficiency is the highest, which is 6.29%.
- iii. The efficiency of inhibitor is increase rapidly during first and second week but it almost same reading at third week and forth week.

As a conclusion, Henna leaves can be used in reduce the corrosion of equipments such as pipes or tanks in industrial wastewater. Based on the literature review, there are many ways to reduce the corrosion where it consumes a lot of money. In this study, henna leaves has the tendency to be a good inhibitor. By using henna leaves, it can decrease the corrosion process happen on the mild steel.

5.3 Recommendation

As for recommendation, further study should be done to study the condition or experimental work procedure which is possible in finding the correct concentration of henna leaves extract to be used to get more effective result. The recommendations for further studies are:

- i. Further study to conduct the study on effect of the pH and temperature.
- ii. Further study to conduct the study with different concentration of henna leaves extract in order to prevent corrosion in industrial wastewater.

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APPENDIX A
TEMPLATE OF DATA COLLECTION

OBJECTIVE 1

Volume of HCl: 200mL Contact Time: 4 weeks

Room Temperature

Concentration of Inhibitor, (g/L)	0	5	15	25	35
Initial Weight, W_1 (g)	143.58	129.45	134.69	122.87	85.07
Week 1, W_2 (g)	137.55	125.13	129.43	118.97	81.60
Week 2, W_3 (g)	137.42	124.11	128.78	117.25	80.64
Week 3, W_4 (g)	137.23	123.11	128.17	116.47	80.06
Week 4, W_5 (g)	137.00	122.95	127.77	116.37	79.97
Weight Loss, WL (g)	6.58	6.50	6.92	6.50	5.10
Inhibition Efficiency, (%)	-	5.02	5.14	5.29	6.00

OBJECTIVE 2

Volume of HCl: 200mL Contact Time: 24hours

Different Temperature

Temperature (°C)	Initial Weight, W_1 (g)	Final Weight, W_2 (g)	Weight Loss, WL (g)	Inhibition Efficiency, (%)
25	92.83	91.12	1.71	1.84
40	141.14	137.80	3.34	2.37
50	80.73	77.06	3.67	4.55
60	79.98	74.95	5.03	6.29