The Utilization of Extract Belimbing Wuluh Leaves (Averrhoa Bilimbi) as Natural Inhibitor Corrosion to Prevent Corrosion on Metal Mild Steel

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Abstract: Corrosion is a gradual destruction of metal, which decrease the quality (degradation) of metal because of their reaction with environment by chemical or or electrochemical in usage time. Extract of belimbing wuluh leaves (Averrhoa Bilimbi) is an organic substances that can be used as a natural inhibitor because it contains tannin that reduce corrosion rate of mild steel in corrosive medium. Tannin in extract of belimbing wuluh leaves is analyzed with two phase, first is qualitative analyze (discoloration from brown to green) and second is quantitative analyze and obtained the tannin level is 0.3924%. Weight loss method is used to test the effectiveness of extract belimbing wuluh leavesas an inhibitor on metal mild steel sized 4 cm x 2,1 cm x 0,2 cm with various of corrosive medium (such as rain water, swamp water, and river water) and corrosion rate test (1 week, 2 weeks, 3 weeks, 4 weeks and 5 weeks). The result of research showed that usage of extract belimbing wuluh leaves as natural inhibitor is more effective in rain water corrosive environment with corrosion rate test in 5 weeks with efficiency 91%.

Index Terms: Belimbing wuluh leaves, tannin, natural corrosion inhibitor, corrosion, mild steel

I. INTRODUCTION

Corrosion is a gradual destruction of material because of their reaction with environment by chemical or or electrochemical. An environment can be influential in the form of acidic, moisture, rainwater, sea water, lake water, river water, and ground water [1].

Heavy Equipments in industry, pipeline,(oil, water, dan gas) that places in outside will be faster to damage because of rain, fog, and another environment factor that carry an oxide substances to cause corrosion to equipments. To prevent spending a big cost, corrosion control will be needed. One of them is provide an inhibitor that prevent a period of immersion in environment.

Inhibitor is a chemical substances that can prevent a corrosion rate effectively if it will be added in small amounts to a koroden (a corrosive environment). Organic inhibitors or known as green inhibitors come from plants or seeds. Plants should be contain tannin, organics acid and amino acids, and alkaloid are known to have the ability to inhibit corrosion [5] Natural inhibitors of plants, which are often used in the form of extracts. The form of the extract has several advantages, including that it is easily obtained from plant parts such as seeds, leaves, skin and stems. In addition, more than one organic product is contained in the extract so that it will strengthen corrosion inhibition [4]

Some sources say that extracts of bedimming wuluh leaves, tea and coffee leaves can effectively reduce the corrosion rate of mild steel in a solution of artificial sea water with CO2 saturated. The effectiveness of extracts of natural ingredients as corrosion inhibitors is inseparable from the nitrogen content contained in its chemical compounds such as belimbing wuluh leaves which contain chemical compounds including oxalate, essential oils, phenols, flavonoids, pectins and tannins [6]

Several factors that influence the corrosion process in the aqueous system include:

1. The ionic component of solution and its concentration
2. pH (acidity level)
3. Oxygen levels
4. Temperature and heat transfer
5. Speed (fluid movement) [2]

Based on the form of damage produced, the cause of corrosion, the environment in which corrosion occurs, as well as the type of material being attacked, corrosion is divided into:

1. *General / Uniform corrosion*
   Caused by chemical or electrochemical reactions that occur uniformly on the metal surface. The effect is that there is thinning on the surface and eventually causes failure due to the inability to withstand the load. This corrosion can be prevented or controlled by selecting materials (including coatings), adding corrosion inhibitors to the fluid or using cathodic protection.
2. *Galvanic corrosion*
   Corrosion caused by a potential difference between two metals in a fluid or conductive and corrosive media. As a result, metals with low corrosion resistance will experience a higher corrosion rate compared to metals that have high corrosion resistance. This corrosion can be prevent by use the same type of material or use a combination of several materials that have similar galvanic properties, using insulation on the connection between metals, and reduce the corrosion characteristics of the fluid using corrosion inhibitors.

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3. *Crevice corrosion*
   Corrosion that occurs due to material deposition in the cracks (especially in the connection).
4. *Pitting corrosion*
   Corrosion phenomenon where the corrosion process occurs in an area on the metal surface which eventually causes a hole in the surface. This corrosion is usually caused by chloride or ion containing chlorine. This corrosion can be prevented by selecting suitable materials and having high resistance to corrosion.
5. *Erosion corrosion*

Corrosion occurs as a result of the high relative movement of corrosive fluids to the metal surface. This process generally takes place in the presence of chemical or electrochemical decomposition on the metal surface..

6. *Stress corrosion*
   Corrosion that occurs due to a combination of load on metal and corrosive media. This corrosion can be occur if the load received by the metal exceeds a minimum stress level.
7. *Crevice corrosion*
   Corrosion that occurs between the gaskets, overlapping joints, screws or grooves formed by sediment impurities or arising from rust products.
8. *Selective leaching*

This corrosion is related to removing one element from a metal mixture. The easiest example is desinification which releases zinc from copper alloys.

A. . Factors Affecting Corrosion

Some environmental factors that can affect the corrosion process include :

1. Temperature

A rise in temperature will cause an increase in the speed of the corrosion reaction. This happens because the higher the temperature, the kinetic energy of the reacting particles will increase so that it exceeds the price of the activation energy and consequently the rate of reaction (corrosion) will also be faster, and vice versa. (Fogler, 1992).

2. Fluid Flow Rate or Stirring Speed

Corrosion rates tend to increase if the rate or velocity of the fluid flow increases. This is because the contact between the reagent and metal substances will get bigger so that more metal ions will release so that the metal will experience brittleness (corrosion). [8]

3. Concentration of Corrosive Materials

This is related to the pH or acidity and alkalinity of a solution. Acidic solutions are very corrosive to metals where the metal in the acidic solution media is more quickly corroded because it is an anode reaction. Whereas alkaline solutions can cause corrosion in the cathode reaction because the cathode reaction is always simultaneous with the anode reaction [7]

4. Oxygen

The presence of oxygen in the air can come into contact with a moist metal surface. So the possibility of being corrosion is greater. In the water (open environment), the presence of oxygen causes corrosion [7].

5. Contact Time

Action inhibitors are expected to make metal resistance to corrosion greater. With the addition of an inhibitor into the solution, it will cause the reaction rate to be lower, so that the inhibitor's working time to protect the metal becomes longer. The ability of the inhibitor to protect the metal from corrosion will be lost or discharged at a certain time, this is because the longer the time the inhibitor will be increasingly discharged by the solution. [3]

B. Mechanism for the Formation of Corrosion Cells

In general, the mechanism of corrosion that occurs in a solution starts from a metal that is oxidized in solution, and releases electrons to form metal ions that are positively charged. The solution will act as a cathode with the most common reaction being H_2 release and O_2 reduction, due to reduced H^+ and H_2O ions. This reaction occurs on the metal surface which will cause peeling due to the dissolution of the metal into the solution repeatedly ([8]

C. Effect of Chloride Ions on Steel Aqueous Corrosions

Corrosion in carbon steel is influenced by the concentration of aggressive ions such as chloride ions (Cl^-). The higher chloride ion concentration will increase the tendency of corrosion. Chloride ions act mostly as ion trigers or aggressive ions because of their ability to destroy the passive layer on the surface of carbon steel and accelerate the rate of corrosion.

Chloride ions are not a scientific element found in water, but are usually added to control the development of aquatic organisms. When dissolved in water, the chloride ion will change to hypochlorous acid (HClO) and hydrochloric acid (HCl), which will reduce the pH value.

Chloride ion is known to have a destructive effect on carbon steel. Most of these ions have the ability to be absorbed on the metal surface and interfere to form a passive layer. Pitting is the main type of attack that occurs due to chloride ions. A small area where Cl-ions are absorbed on the metal surface is an anodic region towards a broad cathodic passive oxide layer. When the process starts, the reaction of hydrolysis of metal ions from an anodic reaction causes a decrease in pH, which prevents repair of the film layer and speeds up the attack. Carbon steel will be corroded in chloride-containing water, especially in the form of uniform corrosion compared to localized attacks.

The effect of chloride ions on the corrosion rate depends on the cation of the salt concentration solution. The difference in corrosion rates in salt solutions such as Lithium chloride (LiCl), Sodium chloride (NaCl), and Potassium chloride (KCl) due to differences in the solubility of oxygen in each salt solution. Thus, the effect of one component concentration can be influenced by other environmental variables on aqueous corrosion.

D. Effect of pH on Aqueous Steel Corrosion

The pH value in water (electrolytes) can differ from the actual pH on the metal surface depending on the reaction that occurs on the surface. Oxygen reduction will produce OH ions - which can increase the pH value, but below the deposit of corrosion products pH values can be suppressed. When the water (electrolyte) pH is moderate (pH = 5), uniform corrosion is the dominant attack which will increase with a decrease in pH. At pH 4 or <4, the protective oxide layer dissolves and is exposed to the metal surface. Corrosion will occur more quickly because the dissolved oxygen level decreases on the metal surface at low pH. Both reactions, hydrogen evolution and oxygen reduction, become cathodic reactions. At an increase in pH above 4, iron oxide is precipitated from the solution to the deposit form. Uniform corrosion suddenly decreases, but under deposit begins to form Fe2O3 on the metal surface. The anodic reactions are as follows :

$Fe + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ + 3e^-$

$Fe + 2H_2O \longrightarrow FeO(OH) + 3H^+ + 3e^-$

$Fe + 3/2H_2O \longrightarrow Fe_2O_3 + 3H^+ + 3e^-$

The deposit is as a barrier to oxygen diffusion to the metal surface. At elevated pH, iron oxide deposits change from a bit adherent at pH 6 to be hard and strong at pH> 8.

Mechanism of steel corrosion in HCl is a high corrosion rate at all acid concentrations at pH <3. The presence of chloride ions serves to accelerate the corrosion rate. The corrosion rate increases with the presence of hydrogen ion concentration (decrease in pH).

The mechanism of the corrosion process based on the variable pH for steel whose corrosion rate increases at very low pH, the rate of corrosion is not pH dependent in a neutral pH range, the corrosion rate decreases with an increase in pH, and finally the corrosion rate increases again at the same high pH. Carbon steel anodic reactions, namely:

$Fe \longrightarrow Fe^{2+} + 2e^-$

It is important that pH affects the corrosion of carbon steel at low pH is not a simple thing. This is because the kinetic equation is related to the corrosion rate. In addition, for example the presence of additional ions such as Cl ions may increase the incidence of cotohous localized attacks, crevice corrosion, and SCC (Stress Corrosion Cracking).

E. Effect of Dissolved Oxygen on Aqueous Steel Corrosion

Corrosion of iron or steel at room temperature requires neutral and alkaline dissolved oxygen to be stable without the presence of oxygen. The process of agitation or stirring can increase oxygen dissolution transport and increase corrosion rate.

The initial increase in temperature increases the rate of corrosion by doubling with a temperature increase of every 30 ° C, but at temperatures> 80 ° C solubility from dissolving oxygen can reduce corrosion rates.

The difference in dissolved oxygen transport results in differences in aeration differential cells, which will result in localized corrosion on the surface of iron or steel at room temperature. Oxygen too often has access variables for different purposes on larger surfaces. A lower pH is found in the anode area (below the rust oxide deposit) while the surrounding is the cathode (high pH) region resulting from the reaction of dissolved oxygen.

When compared with nonferrous metals, such as copper and zinc, the corrosion behavior of carbon steel is slightly sensitive to water quality. This is consistent with the fact that products from anodic reactions in carbon steel are not protective. The corrosion rate in steel is controlled by a cathodic, ie dissolved oxygen supply.

F. Rust Characteristics of Steel

Pure steel consists of white-silver, tough and strong metal. The steel melts at a temperature of 1535oC. In applications rarely use pure steel, usually the steel used contains a number of graphite and other alloying elements. These alloy elements play a role in improving the mechanical properties of steel. Iron forms two important salt series, namely:

1. Iron (II) oxide derived from iron (II) oxide (FeO)

Under conditions of aqueous solution, the iron salts contain Fe2 + cations (iron ion II) which can be easily oxidized to Fe3 + ions (iron ion III) in an atmosphere of neutral, alkaline, or even in high oxygen-containing atmospheric conditions.

2. Iron (III) oxide derived from iron (III) oxide (Fe2O3)

This salt is more stable than iron salt (II). In aqueous conditions, the cation of Fe3 + is light yellow, if the solution contains chloride, the yellow color produced on the surface becomes stronger. Steel can be dissolved into Fe2 + and Fe3 + ions by adding dilute or concentrated hydrochloric acid and dilute sulfuric acid.

The reaction between steel and hydrochloric acid produces iron (II) salts and hydrogen gas, the reaction is :

$Fe + 2H^+ \longrightarrow Fe^{2+} + H_{2(gas)}$

$Fe + 2HCl \longrightarrow Fe^{2+} + 2Cl^- + H_{2(gas)}$

Whereas the reaction between hot sulfuric acid and steel produces iron (III) ions and sulfur dioxide. The reaction is as follows:

$2Fe + 3H_2SO_4 + 6H^+ \longrightarrow 2Fe^{3+} + 3SO_{2(gas)} + 6H_2O$

In addition, white deposits of iron (II) hydroxide (Fe (OH) 2) when reacting with the atmosphere are easy to react with oxygen which ultimately produces reddish brown iron (III) hydroxide. Under normal conditions, Fe (OH) 2 looks like a dirty green precipitate.

G. Corrosion Control and Protection

Because evenly distributed corrosion is relatively easy to measure and predict, failure is relatively rare. Like the occurrence of corrosion that is evenly distributed to the entire surface of metal components, it can practically be controlled by cathodic protection with the use of coatings or paint.

Corrosion has been defined as a decrease in metal quality by electrochemical reactions with its environment. In most practical situations corrosion attacks cannot be prevented, we can only try to control them so that the structure or components have a longer lifetime. Each component undergoes three main stages: design, manufacture and use. Corrosion control is an important role in each stage. Corrosion control can be done in various ways but the most important are:

a. Design modification
b. Environmental modification
c. Providing a protective layer
d. Material selection
e. Cathodic or anodic protection

Corrosion and metal depletion rates are very dependent on the environment. Minor changes in the environment, such as pH, temperature, oxygen solubility, flow rate and the presence of pollution can change the nature and ferocity of corrosion.

Radically. In choosing a control method, special attention must be paid to any environmental changes that may be experienced during the life of the structure, or any possibili ty of dealing with certain malignant environments that occur during manufacture, establishment or maintenance.

Corrosion damage may only appear after a few months, or even several years, that is after something has been detected. Careful examination of the overall structure at the design stage will allow us to predict parts of the system that are likely to be corrosion. Corrosion control aims to regulate the corrosion rate, so that the corrosion rate can be reduced by protection through the addition of an inhibitor in the solution. Protection techniques such as cathode and anode protection, coating, inhibitors, and material selection are often used as the most effective means of corrosion protection.

Control of even corrosion can be done:

1. Selection of corrosion resistant material. Knowledge of corrosion characteristics and corrosion rates in metals and metal alloys as shown in the literature or measured by electrochemical techniques or through metal weight reduction allows good material selection.
2. Solution aggressiveness can be reduced by reducing the chloride content, acidity and / or temperature, inhibiting the flow of the deposit formation process, eliminating the accumulation of hydrolysis of corrosion products, and purifying the pH.
3. Giving an inhibiting element in the solution (inhibitor), but this method must be calculated properly, because if the inhibitor content contained in the solution is not enough then in some parts of the equipment there can be a small hole in the damage.
4. Cathodic protection for equipment used in the marine environment but this method is not always an option that allows for the flow of aggressive chemical processes.

Cleaning the metal surface when possible will reduce corrosion.

There are several principles of corrosion prevention according to which their use is adjusted to the type of equipment, place, and type of corrosive environment. The principles of corrosion prevention are as follows:

a. Corrosive environmental improvement principle
b. The principle of neutralization of coroden substances is such that it is no longer dangerous
c. Surface protection principle by :
    1) Coating with paint (organic coating)
    2) Coating of metal coating, lining, overlay, and clodding
    3) Inorganic coating Wrapping
d. The principle of using the same material that is resistant to certain types of corrosion
e. Use of corrosion inhibitors
f. Cathodic protection and anodic protection (Widharto, 1999: 97).

II. CALCULATION OF CORROSION RATE AND EFFICIENCY OF INHIBITORS

A.Calculation of Corrosion Rate

One of the objectives of corrosion monitoring is to determine the corrosion rate of metals from a structure so that by knowing the corrosion rate we can predict when and for how long the structure can withstand corrosion attacks. Corrosion monitoring techniques can be divided into several methods namely weight loss and electrochemistry (polarization diagram, linear polarization resistance, electrochemical impedance spectroscope, corrosion potential, and electrochemical noise).

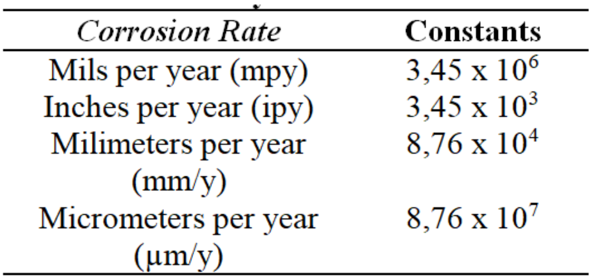
Weight loss method is a method that can be used to obtain corrosion rates. The principle of this method is to calculate the amount of material lost or lost weight after testing the bath according to ASTM G 31-72 standards. By calculating the mass of the metal that has been cleaned from the oxide and the mass is expressed as an initial mass then it is carried out in a corrosive environment such as in seawater for a certain time. After that, the mass is calculated again from a metal after cleaning the metal from the result of the corrosion formed and the mass is expressed as the final mass. By taking some data such as submerged surface area, immersion time and the density of metals tested, a corrosion rate is produced. Corrosion rate equation can be shown in the following equation:

$$\textit{Corrosion Rate} = \frac{KxW}{AxTxD}$$

Information :

K : Constants, lihat pada Tabel 2.1
T : *Time of exposure*
A : Soaked metal surface area (Cm^2)
W : Losing Weight (gram)
D : Density (ρ) = $\frac{m}{PxLxT}$, gr/cm^3 (Bunga, 2008)

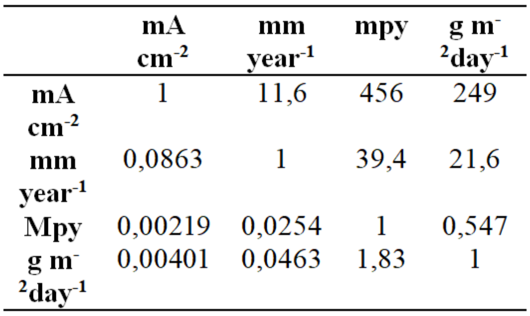
Table 1. The Calculation Calculation of Corrosion Rate by Unit



Corrosion Rate	**Constants**
Mils per year (mpy)	3,45 x 10^6
Inches per year (ipy)	3,45 x 10^3
Milimeters per year (mm/y)	8,76 x 10^4
Micrometers per year (μm/y)	8,76 x 10^7

Sumber : Bunga, 2010

Table 2. Conversion Calculation Corrosion Rate



	mA cm^{-2}	**mm $year^{-1}$**	**mpy**	**g $m^{-2}day^{-1}$**
mA cm^{-2}	1	11,6	456	249
mm $year^{-1}$	0,0863	1	39,4	21,6
Mpy	0,00219	0,0254	1	0,547
g $m^{-2}day^{-1}$	0,00401	0,0463	1,83	1

Sumber : Bunga, 2010

The greater the corrosion rate of a metal, the faster the material is corroded. The quality of corrosion resistance of a material can be seen in the Table.

Table 3. Quality Distribution of Material Corrosion Resistance

Relative corrosion resistance	mpy	Mm/yr	$\mu m/yr$	nm/yr	pm/s
Outstanding	< 1	< 0,02	< 25	< 2	< 1
Excellent	1–5	0,02–0,1	25–100	2–10	1–5
Good	5–20	0,1-0,5	100-500	10–50	20–50
Fair	20–50	0,5–1	500–1000	20–150	20–50
Poor	50–200	1–5	1000–5000	150–500	50–200
Unacceptable	200+	5+	5000+	500+	200+

[3]

Weight loss method is often used on industrial and laboratory scale because the equipment is simple and the results are quite accurate, but from testing with the weight loss method to get a corrosion rate has a weakness. The weakness is that it cannot detect quickly changes that occur during the corrosion process, coupon calculations that cannot be translated directly from the equipment, localization corrosion cannot be seen directly without transfer of coupons from the test site, and forms of corrosion that cannot be detected.

B. Inhibitor Efficiency

In the use of inhibitors can be determined the efficiency of the use of these inhibitors. The greater the efficiency of the inhibitor, the better the inhibitor will be applied in the field. Calculation of efficiency is obtained through a percentage decrease in corrosion rate with the addition compared to the corrosion rate without added inhibitors. This calculation can be described as follows:

Inhibitor Efficiency= $\frac{X_a - X_b}{X_a}$ x 100

Information:

X_a: Corrosion rate without inhibitors(mpy)

X_b: Corrosion rate with inhibitors (mpy)

III. BELIMBING WULUH (*Averrhoa Bilimbi L*)

A. Plant Morphology Belimbing Wuluh (*Averrhoa Bilimbi L*)

Tree characteristics. The small starfruit tree is about 10 meters tall with the base diameter of the stem reaching 30 cm. The trunk is wavy and uneven. Vegetable starfruit leaves are compound leaves as long as 30-60 cm with 11-45 pairs of leaves. The child leaves are green, short-stemmed, oval-shaped to push it with a slightly pointed tip, rounded base, flat leaf edge, 2-10 cm long, 1-3 cm wide.

Belimbing wuluh has compound flowers arranged in panicles, in groups. Acid starfruit flowers, such as kepel, grow out of the stem or large branches. The star fruit of the reed is buni in the form of a square shape, with a length of 4-6 cm. The fruit is yellowish green, runny and if it tastes sour[10]

B. Classification of Belimbing Wuluh Leaves (*Averrhoa Bilimbi L*)

[6] is widely planted as a fruit tree. This tropical American plant can be used to treat various diseases. People take the benefits of starfruit during this time just as syrup, sweets, or cooking spices, whereas traditionally these plants are widely used to overcome various diseases such as cough, diabetes, rheumatism, mumps, mouth sores, toothache, bleeding gums, acne until high blood pressure, besides it can also cure paralysis, improve digestive function, inflammation of the rectum [11]

C. Chemical Content Belimbing Wuluh

Belimbing Wuluh stems contain saponin, tannin, glucoside, calcium oxalate, sulfur, formic acid compounds. Wuluh starfruit leaves contain tannins, sulfur, formic acid, and potassium citrate [5] Starfruit leaves contain tannins while the stems contain alkaloids and polyphenols [1]

[2] showed that extracts of starfruit leaves contained flavonoids, saponins and tannins. Star fruit leaves besides tannins also contain sulfur, formic acid, calcium oxalate and potassium citrate. [6] explained that in addition to tannin belimbing wuluh leaves also contain calcium oxalate peroxidase and potassium citrate. The active ingredient in wuluh starfruit leaves that can be utilized as medicine is tannin.

This tannin is also used as an astringent for both the digestive tract and skin and can also be used as a diarrhea medication. Belimbing Wuluh leaves also contain peroxide compounds which can affect antipyretics, peroxide is an oxidizing compound and its work depends on the ability to release active oxygen and this reaction is able to kill many microorganism.

D. Tannin

Tannins are a group of water-soluble polyphenols with molecular weights between 500 - 3000 gr / mol. Tannins are able to precipitate alkaloids, gelatin and other proteins, form a deep red color with potassium ferrisianide and ammonia and can be precipitated by Cu, Pb and Potassium chromate salts (or 1% chromic acid). Tannins are many and widely distributed substances, so they are often found in plants. Tannins are known to have several properties, namely as astringent, anti-diarrhea, anti-bacterial and antioxidant. The term tannin itself comes from the French language, namely "tanning". At first tannin compounds are better known as "tanning substances" in the process of animal tanning to be made as handicrafts [11]

To distinguish tannins from other secondary metabolites, it can be seen from the properties of the tannins themselves. Tannin properties, among others:

1. Physical properties.
   a. When dissolved in water, tannins will form colloids and will have sour and septic flavor.
   b. When mixed with alkaloids and glatin, precipitate will form.
   c. Tannins cannot crystallize.
   d. Tannins can precipitate proteins from their solutions and form compounds with these proteins so that they are not affected by protiolytic enzymes.

2. Chemical Properties
   a. Tannins are complex compounds that have a mixture of polyphenols that are difficult to separate so that it is difficult to form crystals.
   b. Tannins can be identified using chromatography
   c. Phenol compounds present in tannins have adstrigensia, antiseptic and color-giving action.warna.

3. Properties as metal chelating.

Phenols present in tannins can be biologically useful as metal chelates. The mechanism or process of binding will occur according to the pattern of substitution and the pH of the phenol compound itself. This usually occurs in hydro lyzed tannins, so it has the ability to become a metal chelating agent.

The chelate produced from this tannin can have strong chelating power and can make metal chelate more stable and safe in the body. However, consumption of tannins must be in accordance with levels, because if too little (low levels) will not give effect, but if you consume too much (high levels) can cause anemia because iron in the blood will be chelated by the tannin compound.

E. BelimbingWuluh leaves extract (*Averrhoa Bilimbi L)* as Corrosion Inhibitor

Generally, corrosion inhibitors come from organic and inorganic compounds containing groups that have free electron pairs, such as nitrite, chromate, phosphate, urea, phenylalanine, imidazoline, and amine compounds. However, in reality that this synthetic chemical is a dangerous chemical, the price is quite expensive, and not environmentally friendly, so often small and medium industries rarely use inhibitors in cooling systems, piping systems, and their production water treatment systems, to protect iron / steel from corrosion attacks. For this reason, the use of inhibitors that are safe, easy to obtain, biodegradable, inexpensive, and environmentally friendly are needed.

Inhibitors of extracts of natural ingredients are the solution because they are safe, easy to obtain, biodegradable, inexpensive, and environmentally friendly. Extracts of natural substances, especially compounds containing atoms N, O, P, S, and atoms that have free electron pairs. These elements that contain free electron pairs can later function as ligands that will form complex compounds with metal and steel. Guava leaf extract is expected to be effective as an inhibitor in samples of iron, copper, and aluminum metals in saline solution medium because it contains compounds that can reduce corrosion rates in iron and steel metals.

The mechanism of protection of extracts of natural ingredients against iron / steel from corrosion attacks is estimated to be almost the same as the mechanism of protection by organic inhibitors. The reaction that occurs between Fe2 + metal and corrosive medium of seawater containing chloride ions which decompose from NaCl, MgCl2, KCl will react with Fe and is estimated to produce FeCl2 (Gogot Haryono, 2010). If the chloride ion reacts bigger, then the formed FeCl2 will also get bigger, as written in the following reaction:

$NaCl \rightarrow Na+ + Cl^-$

$MgCl_2 \rightarrow Mg_2 + 2Cl^-$

$KCl \rightarrow K+ + Cl^-$

The chloride ion in the reaction above will attack the iron (Fe) metal so that the iron will be corroded into :

$2Cl^- + Fe^{3+} \rightarrow FeCl_3$

and the reaction between Fe2 + with an extract inhibitor of natural ingredients produces complex compounds. Nitrogen-containing extracts of natural ingredients donate an electron pair to the surface of mild steel metal when Fe2 + ions are diffused into the electrolyte solution, the reaction is:

$Fe \rightarrow Fe^{2+} + 2e-$ (release electron) and

$Fe^{2+} + 2e^- \rightarrow Fe$ (receive electron).

The products formed above have a high stability compared to Fe alone, so that the iron / steel samples given inhibitors of natural ingredients extract will be more resistant (protected) to corrosion.

IV. WATER

Water is a major need for the life process on this earth. There will be no life if on this earth there is no water. Relatively clean water is highly coveted by humans, to be used as drinking water, bathing, washing, industrial needs, sanitation of the city, and for agricultural purposes and so on. Water in normal conditions will not be colored, so it looks clear and clean [10]

A. Types of Water

a. Rainwater

Rainwater content itself depends on the geological conditions, population, and activities carried out by humans in the area. So that the content of rainwater will vary in each place. For example, in open sea areas to areas close to the coast, rainwater will contain salt, CO2 and be acidic. While rainwater on land has far less salt content. Especially in densely populated cities, it is likely that the rainwater content comes from the remnants of pollution. If it rains in a clean environment, the mass of impurities in rainwater is also small, but if it rains in an environment where the environment is not clean, there will be a lot of impurity in it. Checking the pH of rainwater can be one way to determine the effect of corrosion rates.

Basically the content of rain water comes from the reaction of substances in the atmosphere with water droplets passing through it. Generally consisting of 99.9 percent of H2O mass and the rest are substances that are mixed with rainwater, in the form of soluble solids and gas[3]

b. Swamp Water

Swamp is a land with relatively flat slope with naturally occurring puddles that occur continuously or seasonally due to natural drainage that is hampered and has physical characteristics: sunken land surface shape, sometimes peat, chemical characteristics: lowest water acidity and biological characteristics: there are swamp fish, swamp plants and swamp forest.

Swamps are divided into two types, namely: tidal swamps located on the beach or near the beach, in the estuary or near the river mouth so that the tides and non-tidal swamps or inland swamps or swampy swamps are located further away from the beach so not affected by the ups and downs of sea water. Swamp or wet land is a swamp is a scientific waterlogging area that occurs continuously or seasonally due to obstructed drainage and has special physical, chemical and biological characteristics.[2]

From previous research, swamp water and swamp mud have a content that causes corrosion in concrete bones. Water and swamp mud contain organic matter, high humus so the pH is low which results in acidic swamp water. The nickname of laymen against corrosion is a major cause of damage to materials which are generally made of metal, causing losses. [4]

d. River Water

The river is a natural waterway that flows into the ocean, lake or sea, or to another river. In some cases, a river simply flows into the ground before finding another water body. By river is the usual way for descendant rainwater to flow to sea or large water reservoirs such as lake.

The river consists of several parts, starting from the eyes of the water that flows into a tributary. Some tributaries will join to form the main river. The water flow is usually bordered by the channel with the base and cliff on the left and right. The end of the river where the river meets the sea is recognized as the river mouth.

Some studies on the river that empties into the coast of Sumatra have decreased, especially in the river Siak is quite low with a range of 0 - 2.4 mg / l so that it is categorized as heavily polluted. In this case it will be seen the effect of salinity on the increase in dissolved oxygen, especially in the bermura river on the east coast of Sumatra. The highest dissolved oxygen concentration of the six rivers that flow to the east coast of Sumatra was found in the musi river with a concentration of 5.12 mg / l. Oxygen concentration is one of the factors that influence corrosion rate.[4]

V. METHODS

A. Time and Places

Research on the utilization of Belimbing Wuluh leaves extract (Averrhoa Bilimbi) as a natural corrosion inhibitor to prevent corrosion in mild steel metal which varied various corrosive medium and soaking time was carried out in the Chemical Engineering Laboratory, Faculty of Engineering, Muhammadiyah University, Palembang.

B. Tools and Materials Used

a. Tools used

1. Corrosion Test Equipment

Metal *mild steel*	6 pcs
Glass	6 pcs

2. Tools for analysis

Beaker Glass	1 pcs
Analytical Balance	1 pcs
Blender	1 pcs
Reagen Glass	1 pcs
Filter Paper	1 sheet
volumetric flask 100 mL	1 pcs
Oven	1 pcs
Spatula	1 pcs
Termometer	1 pcs
pH Meter	1 pcs
Buret	1 pcs
Piknometer	1 pcs
Erlenmeyer& Beaker Glass	3 pcs

b. Materials Used

1. Materials for making extracts

Belimbing wuluh leaves	1 kg
Etanol 96%	750 ml

2. Materials for making Corrosif media

Rainwater	2 liter
Swamp water	2 liter
River water	2 liter
Aquades sufficiently	

3. Materials for tanninn analysis

Ocsalat acid	0,63 gram
Indigocarmin	3 gram
$KMnO_4$	3,2 gram
H_2SO_4 p.a	10 ml
$FeCl_3$	5 gram
Aquades sufficiently	

c.. Experiment Variable

The variables applied in this study are the types of water used as corrosive media and soaking time, as well as the limitations of the problem in this study. The effect of media type and immersion time on corrosion rate will be evaluated to determine the effect of starfruit leaf extract in reducing metal corrosion rate. The type of solution used was musi river water, rainwater, and swamp water, and the immersion time was around 5 weeks with a 7-day intervals of data retrieval.

C.Trial Procedure

a.Sample Preparation

1. Prepare the main ingredients (leaves of starfruit), as much as 1 kg.
2. Separating leaves from twigs and other impurities.
3. Clean the leaves of starfruit by using water 2 times then drained.
4. Cut the leaves of starfruit to a size smaller than the original size.
5. Smoothing starfruit leaves which have been cut into small pieces, until obtained starfruit leaves powder.
6. Drying starfruit leaves powder in the shade without being exposed to direct sunlight for 5 days.
7. Weighing 150 grams of starfruit leaves which are used as the main ingredients of the extraction process

b. Belimbing Wuluh Leaf Extraction with Maseration Method

1. repare 1 reagent bottle, as an extraction process reactor.
2. eigh 150 grams of starfruit leaf powder, then put starfruit leaves powder into a reagent bottle.
3. dd 750 mL of 96% ethanol to the reagent bottle, and then close the reagent bottle tightly.
4. ilence mixture of starfruit leaves ethanol for 5 days, with stirring done once a day.
5. n the 6th day the mixture of starfruit leaves powder was filtered, using filter paper. From the screening process, two parts of the mixture are obtained, namely filtrate and residue.
6. he obtained filtrate is 690 mL, then evaporated at a temperature of 60-70oC for 50 minutes.
7. rom the evaporation process found 679 mL of bio-inhibitor corrosion leaves.

c. Preparation Metal *Mild Steel*

1. mooth the surface of mild steel metal samples using sandpaper.

2. The smooth surface is then washed with HCl and distilled water.
3. Dry in an oven at 110oC for 2 hours.

d. Immersion of Mild Steel Metal in Corrosion Media without Inhibitors

1. The samples that have been prepared are each soaked in corrosive media (river water, swamp water, and rainwater).
2. Soaking is done for 5 weeks, and weighing each sample's weight every 1 week.
3. Measuring the pH of the solution using a pH meter.

e. Soaking Mild Steel Metal in Corrosion Media with Inhibitors

1. The prepared samples were each soaked in corrosive media (a solution of rainwater, swamp water and river water) which had previously been added with 5 ml of starfruit leaf extract.
2. Soaking is done for 5 weeks, and weighing each sample's weight every 1 week
3. Measuring the pH of the solution using a pH meter.

D. Tannin analysis on Belimbing Wuluh leaf extract

a. Reparation of Reagent Solution

Indigocarmin solution

A total of 3 grams of indigocarmin were dissolved in 250 ml of distilled water and heated. After cold, add distilled water to one liter.

$KMnO_4$ 0,1 N solution Weighing 3.2 grams of KMnO4 then dissolved in one liter of distilled water. Then boil for 10-15 minutes. After that filtered and diluted 1 liter of distilled water, then stored for one night. The standard KMnO4 solution needs to be standardized before use [6]

b. KMnO4 Solution Standardization

- Weigh 0.63 grams of oxalic acid crystals and dissolve them in 100 ml of distilled water.
- Take 25 ml of oxalic acid solution and add 5 ml of H2SO4 p.a then heated to 70oC.
- Then in hot conditions titrated with a standard KMnO4 solution to purple and the permanganate droplets are no longer lost, then the volume of the titration is recorded. Repeat the titration up to three times.

Reaction :

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 + 10CO_2 + K_2SO_4 + 8H_2O$$

The normality of the KMnO4 standard solution is calculated using the formula :

$$KMnO_4 = \frac{\frac{W(mg)}{BM} x\ 2\ x \frac{25}{100}}{V\ (mL)}$$

Information :

W : Weighing the weight of crystalline oxalic acid (mg)

BM : Molecular weigh (126)

v : Titration volume

25/100 : Dilution factor

2 : Electron valence of oxalic acid

E. Qualitative Test of Tannin Levels

1. Weighing 10 grams of starfruit extract, then put it in a prepared beaker.
2. Add 10 mL of aquadest and 1 mL of HCl into a beaker, which contains extracts of starfruit.
3. Heating until the solution in the beaker boils, with a temperature of 100oC.
4. Add 3 drops of FeCl3 solution, until the green solution will be form.

F. Quantitative Test of Tannin Levels

1. Considering 1.5 grams of starfruit extract extract then put into a 100 ml glass beaker and then add 50 ml of water. Heating at a temperature of 40 - 60oC for 30 minutes. After being cold, the solution is filtered and put into a 250 ml volumetric flask and added to distilled water until the boundary mark.
2. From the above solution, 25 ml is taken into the erlenmeyer and added 20 ml of indigocarmin solution then titrated with standard KMnO4 solution, each time adding 1 ml of KMnO4 until the color changes from blue to green then titrated by dropping to green become golden yellow.
3. Determination of blank is done by piping 20 ml of indigocarmin solution into erlenmeyer and titrating until the color changes from blue to green then titrated by dropping until the green color becomes golden yellow.
4. Tannin levels can be calculated using the following formula :

$$\%Tannin = \frac{10(A-B) x\ N\ x\ 0{,}00416}{Sampel\ (gram)}\ x\ 100\%$$

Keterangan :

A : volumetannin titration (mL)

B: volume blanko titration (mL)

N : standart normalitas $KMnO_4$ (N)

10 : Dilution factor

1 mL $KMnO_4$ 0,1 N:equal with 0,00416 gram *tannin*[4]

a. Density Analysis on Belimbing Wuluh Leaf Extract

1. Weigh an empty picnometer using an analytical balance.
2. Fill the empty picnometer with leaf extract of twentieth fruit.
3. Considering a picnometer containing a leaf extract of twentieth fruit.
4. Calculating the density of leaf extracts using formula :

$$\rho = \frac{m}{v}$$

Information :

m :The difference in picnometer mass + Belimbing waluh leaves extract and empty picnometer (gram)
V : Volume piknometer (Cm^3)

VI. RESULTS AND DISCUSSION

A.Research result

Based on experiments that have been carried out obtained extract of starfruit leaves from the extraction process by maceration method using 96% ethanol as a solvent, so that the tannin content is obtained as follows:

Table 4. Belimbing Wuluh Leaves Extraction Results Using Ethanol Solvents

Volume Ekstrak (mL)	Tannin Level (%)	pH
679	0,3924	3,11

Based on research that has been carried out on the corrosion rate on mild steel plates using rainwater, swamp water and also river water as a soaking medium and with varying immersion times. The results of the calculation of the corrosion rate can be seen in the following table :

Table 5. Corrosion Rate in Mild Steel Plates with the Addition of Natural Inhibitors

Medium	Time	Mass (gram)		Corrosion Rate		
	Weeks	Early	End	mpy	g/m^2day	g/m^2week
Rainwater	1	16,1645	15.6645	511.3210	279.6926	1957.848
	2		15.5105	511.3315	279.6984	1957.889
	3		15.3565	354.0970	193.6911	1355.838
	4		15.2025	301.6856	165.022	1155.154
	5		15.0485	275.4798	150.6875	1054.812
River Water	1	16,1645	15.4216	859.3123	542.0868	4946.074
	2		15.2676	821.8376	449.5452	3146.816
	3		15.1136	509.3501	278.6145	1950.302
	4		14.9596	405.1876	221.6376	1551.463
	5		14.8056	353.1063	193.1492	1352.044
Swamp Water	1	16,1645	15.0934	368.3376	201.4807	1410.365
	2		14.9394	1241.3851	679.0377	4753.264
	3		14.7854	719.1239	393.3608	2753.525
	4		14.6314	545.0368	298.1351	2086.946
	5		14.4774	457.9932	250.5223	1753.656

Table 6. Corrosivity Rate in Mild Steel Plates without the Addition of Natural Inhibitors

Medium	Time	Mass (gram)		Corrosion Rate		
	Weeks	Early	End	mpy	g/m^2day	g/m^2week
Rainwater	1	16,1645	15.6685	2620.52	1433.424	10033.97
	2		15.4117	2620.574	1433.454	10034.18
	3		15.2577	3131.906	1713.153	11992.07
	4		15.1037	3089.295	1689.844	11828.91
	5		14.9497	3125.514	1709.656	11967.59
River Water	1	16,1645	14.7957	2998.96	1640.431	11483.02
	2		14.6417	1968.265	1076.839	7537.871
	3		14.4877	2000.585	1094.32	7660.239
	4		14.3337	2075.154	1135.109	7945.764
	5		14.1797	2035.739	1113.549	7794.844
Swamp Water	1	16,1645	13.2557	408.0426	223.1993	1562.395
	2		13.1017	3873.337	2118.716	14831.01
	3		12.9477	3847.77	2104.73	14733.11
	4		12.7937	3864.814	2114.053	14798.37
	5		12.6397	3850.966	2106.479	10033.97

Table 7. pH Medium Solution As A Media Soaking Mild Steel

Medium Solution	Time Weeks	pH	
		without natural inhibitors	with natural inhibitors
Rainwater	0	5,6	6,1
	1	6,05	6,83
	2	6,09	7,09
	3	6,13	7,56
	4	6,17	7,78
	5	6,21	7,83
River Water	0	4,8	5
	1	4,94	5,63
	2	4,86	5,51
	3	4,78	6,49
	4	4,7	6,52
	5	4,62	7,34
Swamp Water	0	2,7	3,84
	1	2,64	4,43
	2	2,89	4,53
	3	3,14	5,62
	4	3,39	6,04
	5	3,64	7,85

VII. DISCUSSION

Based on experiments that have been carried out found extract of starfruit leaves from the extraction process by maceration method using 96% ethanol as a solvent, so that the extract volume was 679 mL, with tannin content of 0.3924% and pH of extract of 3.11. The tannin content in the extract of starfruit leaves was analyzed in two stages, namely qualitative tannin analysis and quantitative methods. For qualitative tannin analysis, it was carried out by weighing 10 grams of starfruit leaf extract, 10 mL of distilled water, and 1 mL of concentrated HCl. Then it is heated to boiling. After boiling, a Ferriclhoride ($FeCl3$) solution is added. After adding $FeCl3$ solution, the solution then changes color from light brown to clear green. These color changes indicate that there is tannin content in extracts of starfruit leaves obtained from the extraction process by maceration method.

For quantitative tannin analysis, titrimetric analysis is done by using $KMnO4$ solution as titrant. Based on the data obtained from the titration process, then obtained tannin levels found in the extract of starfruit leaves, by substituting (combining the equation) the data obtained into the formula for determining tannin levels, so that the tannin content in the extract of starfruit leaves on average is 0 , 3924%.

A. Corrosion rate is based on the duration of immersion with a comparison of the immersion media

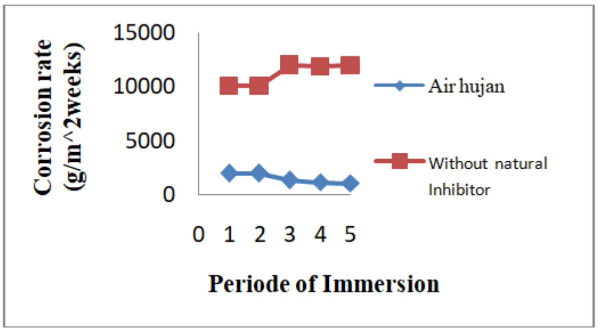


Figure 1. Effect of immersion time on the mass of mild steel lost in rainwater

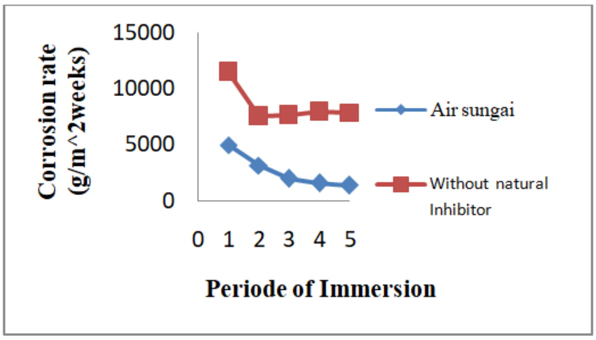


Figure 2. Effect of immersion time on the mass of mild steel lost in river water

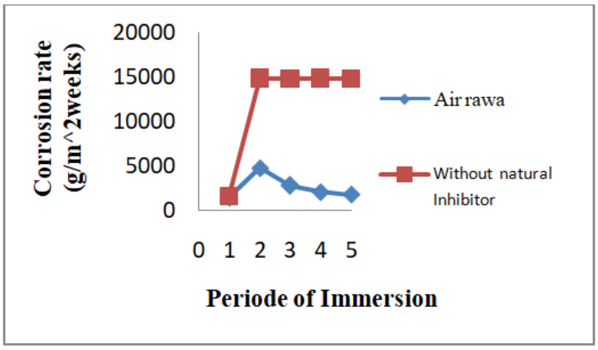


Figure 3. Effect of immersion time on the mass of mild steel lost in swamp water

resistance of steel used. Because the more mass of steel is lost, the corrosivity of the steel is smaller. With the addition of inhibitors in the form of wuluh starfruit leaf extract, it was able to reduce the corrosion rate. This is very clearly seen in the range between soaking media using natural inhibitors and without the use of natural inhibitors. Based on the images and calculations, the optimum conditions of the natural inhibitor efficiency in the rainwater solution were obtained in the fifth week, which was 91%.

VIII. CONCLUSION

Based on the results of the research, it can be concluded as follows:

1. The tannin content obtained from the extraction process of starfruit leaves with maceration method was 0.3924%, with a pH of 3.11.
2. The extract of starfruit leaves used as a natural corrosion inhibitor with a total of 5 mL was able to inhibit the corrosion rate in the studies that have been tested.
3. The effect of soaking time, the longer the immersion time is, the more weight of the mild steel plate is reduced.

The difference in corrosion rates in media added with natural inhibitors and without natural inhibitors can be clearly seen. In each immersion media, media that is not added to natural inhibitors will lose weight from mild steel plates greater than the media which is added by natural inhibitors. Thus, it can be seen that the corrosion rate of a medium that has not been added to natural inhibitors is greater than the corrosion rate found on the plate where the immersion media is added to the inhibitor.

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