



vol. 16 / 2023



The 7th International Conference on Science Technology

organized by
Faculty of Social Science and
Law Universitas Negeri Manado and
Consortium of International Conference
on Science and Technology

The Innovation Breakthrough in Digital and Disruptive Era

THE INFLUENCE OF ADDITION MAJA FRUIT PEEL EXTRACT AS INHIBITOR ON THE CORROSION RATE OF STAINLESS STEEL AND CARBON STEEL

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Abstract. Corrosion can cause serious damage, such as a piece of equipment or a decrease in tool life. The materials used in an industry, its use can be seen in factory flow pipes that carry a substance, which is one of the factors causing corrosion. The aim of this research is to determine the performance of maja rind extract as an inhibitor of stainless steel and carbon steel corrosion rates, to determine the inhibition efficiency of maja rind extract in controlling the corrosion rate of stainless steel and carbon steel. Method use in this reasearch extraction and polarization. The best concentration in controlling the corrosion rate of SS 304 was obtained at 100 ppm with a corrosion rate of 0.00963 mpy, for SS 316 it was obtained at 100 ppm with a corrosion rate of 0.00521 mpy, while on steel plate it was obtained at 100 ppm with a corrosion rate of 0.00774 mpy. The best inhibitor efficiency on SS 304 can reach 97.6% with the best concentration of 100 ppm, on SS 316 it can reach 99.4% with the best concentration of 100 ppm, and on steel plate it can reach 98.84% with the best concentration of 100 ppm.

Keywords: Maja Fruit Peel Extract, Corrosion, Stainless Steel, Carbon Steel

1 Introduction

Indonesia, which makes the industrial sector the foundation of the country's economy, of course has a problem, namely the use of metals which can trigger corrosion. Corrosion events can cause serious damage, such as damage to a piece of equipment or a decrease in tool life. Corrosion, also known as rusting, is the process by which a material breaks down because it reacts with its environment. The materials used in an industry also vary, starting from aluminum, carbon steel, stainless steel or other alloys. Its use can be seen in factory flow pipes that carry a substance, which is one of the factors causing corrosion. One of the prevention of corrosion is the addition of inhibitors. Inhibitors are substances that are added to an environment in small concentrations and can control the corrosion rate effectively. Corrosion inhibitors are typically used to prevent acid corrosion, whereas biocides (or bactericides) are used to prevent the growth of bacteria colonies that cause corrosion [1]. Corrosion inhibition is the most cost-effective, practical, and convenient method of controlling corrosion on metals in an aqueous environment. Corrosion inhibitors regulate both metal dissolution and acid intake. Inhibitors provide a protective barrier on the metal surface and interact with anodic or/and cathodic reaction sites to reduce oxidation or/and corrosion reactions [2]. In general, inhibitors are divided into two types, namely organic inhibitors and inorganic inhibitors [3]. Due to demonstrated synergistic effects that improve their performance, commercial inhibitor formulations almost never use a single compound [4].

Acetylenic alcohols, alkenyl phenones, aromatic aldehydes, nitrogen-containing heterocyclics, quaternary salts, and condensation products of carbonyls and amines are examples of regularly employed inhibitors. However, these inhibitors are only effective at high concentrations and are hazardous to the environment. As a result, it is critical to look for nontoxic, environmentally safe, and effective organic corrosion inhibitors for acidifying oilfield systems. Natural plant extracts are becoming useful in this area [5].

Maja fruit (*Aegle Marmelos* (L.) Corr.) is often wasted because the flesh cannot be eaten, but it can be used as a corrosion control because it contains organic compounds, namely tannins. Tannins are compounds with -OH groups which can react with metals [6].

Based on research conducted by Ludiana (2012), the corrosion rate of carbon steel can be inhibited by using tea leaf extract which contains tannins. Carbon steel with 0% inhibitor concentration has the greatest corrosion rate, after administration of inhibitors with various concentrations the corrosion rate value decreases. The optimum concentration of tea leaf extract as an inhibitor was 4% with an efficiency of 74.32% on the third day and 73.41% on the sixth day, whereas at a tea leaf extract concentration of 5% the corrosion rate increased again because NaCl formed

metal bonds with ions. From these data, it appears that tea leaf extract can be used as a corrosion rate inhibitor.

Another research carried out by Utomo (2018), maja fruit peel extract can be used to inhibit the corrosion rate of soft steel. Testing the corrosion rate in an environment of 0.1 M H₃PO₄ and water using the weight reduction method. The inhibition efficiency in aqueous media increased with the increase in the concentration of the added inhibitor, which reached 45%, but tended to be constant when the addition of inhibitor was above 200 ppm. Another medium used was 0.1 M H₃PO₄ with an inhibition efficiency of up to 57% with increasing inhibitor concentration, but became constant at inhibitor concentrations above 300 ppm.

In this study, the type of inhibitor that will be used is an organic inhibitor made from maja fruit which is often not used and thrown away. According to Fatmawati (2015), young and old maja fruit can be used to reduce corrosion in samples in the form of metal crescents. Old maja fruit is more effective in reducing corrosion on the sample surface than young maja fruit. This difference in effectiveness is influenced by the compound content contained in the two maja fruit.

Based on the description above, natural ingredients which generally contain tannins cant was taken by extraction using a maceration process with modifications. The first thing to do is to prepare maja fruit peel extract. The process aims to extract the extract contained in the rind of the maja fruit. After obtaining the results of maja rind extract, coating using the extract was carried out on stainless steel and carbon steel that had been prepared beforehand and using predetermined variables. The process is continued using a potentiostat, which aims to find the corrosion rate of stainless steel and carbon steel.

2 Literature Review

2.1 Theory Study

2.1.1 Corrosion

Corrosion is defined as the destruction or damage of a material due to reaction with its environment [7]. Corrosion is also defined as the reverse reaction of metal purification due to a decrease in the quality of the metal so that the metal becomes damaged quickly [8].

According to Afandi, 2015, corrosion can occur if there are any of the following:

1. Anode

Areas that arise corrosion due to oxidation reactions $M \rightarrow M^+ + e^-$

2. Cathode

The area that captures electrons so that the reduction reaction occurs

3. There is a relationship

Where current flows from the cathode to the anode

4. Electrolyte solution

A solution that can conduct an electric current that is corrosive because it contains ions.

2.1.2 Factors Affecting Corrosion

Things that affect the occurrence of corrosion:

1. Temperature, the higher the temperature, the faster the chemical reaction, the faster corrosion will occur
2. Flow speed, if the flow rate is faster it will damage the film layer on the metal, it will accelerate corrosion because the metal will lose the layer.
3. pH, the optimal pH, the faster corrosion will occur
4. Oxygen levels, the higher the oxygen level in a place, the easier the oxidation reaction will occur, which will affect the corrosion reaction rate.
5. Humidity [9].

2.1.3 Maja Fruit

Aegle marmelos (L.) Corr.a plant commonly known as Maja has various designations in each region, including, Mojo or Mojo legi (Java), Maos (Madura), Bilak (Malay), and Kabila (Alor, Nusa Tenggara).

Maja fruit can be found in Southeast Asia and South Asia. The chemical ingredients contained in maja include fatty substances and flying oils which contain linolen. The meat contains 2-furocoumarins-psoralen and marmelosin (C₁₃H₁₂O₃). The fruit, roots and leaves are antibiotic. Other ingredients namely pectin, saponins, and tannins. [10]. Based on Veronika's research (2016), maja fruit can contain tannins up to 3% with details on dry skin which has been extracted with ethanol to produce 2.2% and to fresh skin with the same solvent to produce 3%.

2.1.4 Corrosion Rate Analysis Method

There are several methods of corrosion analysis that are often used, namely Thickness Measurement Method, The Weight Loss Method, and Polarization Method [12].

Table 1. The advantages and disadvantages of the corrosion rate analysis method

Method	Excess	Lack
Weight Loss	1. Simple and low cost	1. Cleaning, weighing, and microscopic checking are carried out on a lab scale
Electrical Resistance	1. Results are easy to interpret 2. The technology is well supported by commercial suppliers	1. Only for the observation of uniform corrosion, while local corrosion is usually more common in industry 2. Less sensitivity
Polarization	1. Measurement takes a short	1. Only on the principle of

	time	uniform corrosion
	2. High sensitivity	

[13]

2.1.5 Corrosion Rate Calculation

The corrosion rate is expressed by the amount of metal that has decreased in quality per unit time on a surfacemiles per year(mpy). The equation can be written as:

$$mpy = \frac{434W}{\rho AT} \quad (1)$$

Information :

W = mass of corroded metal (mg)

ρ = density of the material used (g/cm³)

A = area of material used (cm²)

Q = contact time (hours)

where the value of 1 mils is equal to 0.001 inch [14].

2.2 Theoretical Basis

2.2.1 Potentiostat

Potentiostat is a tool that can be used to calculate the corrosion rate of an object. Potentiostats can be used with the specified variable i.e. cell potential. The elements contained in the potentiostat include standard electrodes, working electrodes, and auxiliary electrodes with their respective functions namely as a reference for cell potential, coupons to be analyzed, and as an assistant for the reaction. The potentiostat can be used to calculate the corrosion rate by the Tafel extrapolation method. Extrapolation is carried out on curves where there is potential for E_{corr} corrosion. After that, the intersection with the coordinates (I_{corr}, E_{corr}) is obtained so that the value of the corrosion current can be known. The corrosion current obtained is used to calculate the corrosion rate. I_{corr} is the measured corrosion current [15].

In addition, there is a polarization resistance method that is used to determine the corrosion rate. The mechanism is that current is used to produce a polarization curve on an object whose corrosion rate is calculated. The polarization curve is a function of the potential change from the current value used. The positive direction current used for the potential on the metal surface is referred to as anodic polarization, whereas if the negative direction current is used for the potential on the metal surface it is referred to as cathodic polarization [16]. The polarization method is used to calculate corrosion resistance. Corrosion resistance in question is the coupon's ability to withstand corrosion in an environment. The calculation obtained is the polarization resistance parameter, R_p, which serves to calculate the corrosion current, I_{corr}, so that the corrosion rate can be calculated.

The relationship between R_p, I_{corr}, and the Tafel constant is shown by:

$$\frac{\Delta E}{\Delta i} = R_p = \frac{\beta_a \beta_c}{2.3(I_{corr})(\beta_a + \beta_c)} \quad (2)$$

Information :

R_p = slope of the polarization curve

B_a = anode tafel constant

B_c = cathode tafel constant

i_{corr} = corrosion current

Then the corrosion rate can be calculated as follows:

$$CR(mpy) = 0,13I_{corr} \frac{EW}{A \cdot \rho} \quad (3)$$

Information :

mpy = milli-inch per year

E_w = equivalent weight

A = coupon area (cm^2)

ρ = density of material(g/cm^3)

[15]

2.2.2 Tannins

Tannins are active compounds of secondary metabolites which are known to have several properties, namely as an astringent, anti-diarrhea, anti-bacterial and antioxidant. Tannins are a very complex component of organic matter, consisting of phenolic compounds which are difficult to separate and difficult to crystallize, precipitate proteins from their solution and combine with these proteins. Tannins are divided into two groups: hydrolysable tannins and condensed tannins. Tannins have complex biological roles ranging from protein precipitators to metal chelating. Tannins can also function as biological antioxidants [17].

Tannins which act as antioxidants can inhibit the rate of corrosion by preventing oxidation from occurring. Tannins can bind heavy metals because they contain phenolic compounds which have $-OH$ groups. Tannins are soluble in non-polar compounds such as water and ethanol. Phenol compounds in tannins can bind free radicals from the damage of metal ions [18]. Tannins can interact with Fe ions in two ways, namely:

- a. Formation of complex compounds between tannins and Fe^{2+} ions which produce ferrous-tannates where these compounds are easily oxidized to become ferric-tannates
- b. Tannins can cause reduction reactions resulting in the formation of complex compounds between tannins and Fe^{3+} ions to become Fe^{2+} so that ferrous-tannate compounds are formed and can be oxidized to ferric-tannates [19].

2.2.3 Inhibitors

Corrosion inhibitor is a chemical substance which, when added to an environment, can reduce the corrosion rate that occurs in that environment to a metal in it. According to the basic ingredients of manufacture, corrosion inhibitors can be divided into two types:

1. Inhibitors made of inorganic materials
 Inhibitors that contain synthetic chemicals and are quite effective in inhibiting the rate of corrosion but are toxic.
2. Inhibitors made from organic materials
 Organic corrosion inhibitors are corrosion inhibitors derived from natural materials available in nature, organic inhibitors are non-toxic, inexpensive, readily available in nature, easily renewed and do not damage the environment.

The adsorption process occurs in organic inhibitors which will form a protective layer on the metal surface. The process is divided into:

a. Physisorption (physical adsorption)
 The surface of the metal and the inhibitor will experience electrostatic attraction resulting in adsorption events.

Negatively charged inhibitors (anions) will be more easily adsorbed on metal surfaces that have a positive charge (cations), but if the inhibitor is a cation molecule then the molecule will be combined with anion molecules thereby slowing down the cations on the metal. The advantage of inhibitors with this process is that adsorption events occur briefly, but unfortunately they are easily removed from the metal surface.

b. Chemisorption
 The surface of the metal and the inhibitor will experience a charge handover event between the molecules.

The chemisorption process takes longer than physisorption, but when the temperature increases, the adsorption and inhibition processes also increase. The chemisorption process is more effective than the others because the reaction is irreversible when charge transfer occurs.

c. Film forming
 The metal surface will react with adsorbed inhibitor molecules and form a thin layer or polymer film. If the film formed sticks to the metal surface, the inhibition process can be called effective, preventing access of the solution to the metal surface [19].

2.2.4 Factors Affecting Corrosion Rate

The following are several factors that affect the corrosion rate in seawater media, namely:

1. Salinity
 The content of salt or salinity in sea water is different from fresh water. This is what causes the electrical conductivity to increase thereby facilitating the process of ion exchange between the metal surface and water or air resulting in corrosion [21].
2. conductivity
 Chloride ions (Cl^-) present in seawater can increase the conductivity of the solution so that the corrosion rate will be faster [22].
3. Inhibitors
 Inhibitors added in a certain amount to the metal can cause the metal to be more resistant to water or air reactions so that the corrosion rate occurs lower [16].
4. metal content
 Alloys with Cr content are more difficult to corrode. Stainless steel with more Cr is more resistant to corrosion [23].

2.2.5 Stainless Steel

Stainless steel or stainless steel is an alloy of steel with chromium with a minimum content of 11% by weight. The passive layer of chromium contained in

stainless steel can prevent corrosion, so that stainless steel has strong resistance so that it is not easily corroded, 13 – 26% chromium is added. The passive layer of chrome that is formed is very thin, but if it is scratched it will quickly form a new layer. This passive layer (Cr₂O₃) can also be found in other metals such as titanium and aluminum [24].

According to Outokumpu (2013), SS 304 stainless steel contains the following contents:

Table 2. Elemental content in SS 304

Element	Content (%)
C	0,05
cr	18,1
Ni	8,3

Stainless Steel 304 is the type most often found in daily activities. In addition, it is also found in various food, mining, pharmaceutical, and chemical industries. Its corrosion resistance, affordable price, and versatility make this type the most widely used. The mechanical properties of SS 304 are 646 MPa in tensile strength, 50% elongation, and 270 MPa in yield strength [24].

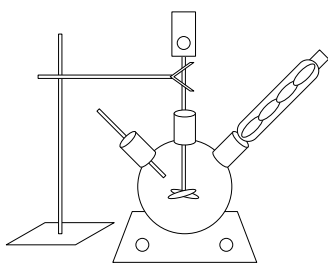
3 Research Methodology

3.1 Materials used

As for the materials used in this study, namely maja fruit obtained from the Trowulan Museum, Mojokerto; 96% Ethanol, Sodium Chloride and Aquadest purchased from PT. Bratachem, and sandpaper. Stainless Steel 304; 316; and Carbon Steel obtained from UPN Veteran East Java.

3.2 The Tools Used

1. Polarization Toolkit



Information :

1. Stative
2. Clamps
3. Stirring motor
4. Thermometer
5. Three neck pumpkin
6. Condenser
7. Heating Mantle

Fig 1. Series of Extraction Tools

2. Polarization Toolkit

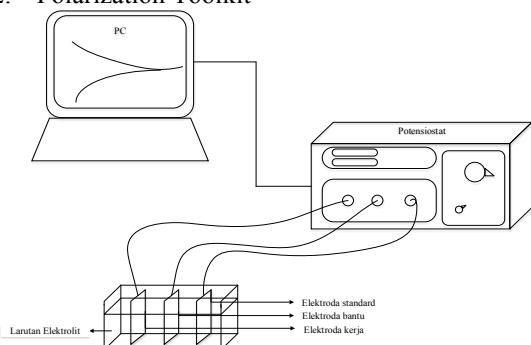


Fig 2. Series of Polarization Tools

3.3 Research Variables

3.3.1 Defined conditions

A. Extraction

The ratio of maja fruit to solvent = 1 : 5

Extraction Temperature = 60°C

Extraction Time = 3 hours

Stirring Speed = 200rpm

B. Potentiostat

Coupon Size = 1x1cm

Standard Electrodes = Ag – AgCl

Auxiliary Electrode = Platinum (Pt)

3.3.2 Variables Used

Concentration Inhibitors (0 ppm; 100 ppm; 200 ppm; 300 ppm; 400 ppm; 500 ppm)

Coupon Type (SS 304, SS 316, Carbon Steel)

3.4 Research Procedure

3.4.1 Preparation of Maja Fruit Peel Extract

Maja fruit is separated between the outer skin, inner skin, fruit flesh, and seeds. Then the outer skin that has been separated, dried in the sun to obtain a constant weight. The dry outer skin is ground to form a powder. Maja fruit peel powder is put into a three neck flask and then extracted.

3.4.2 Preparation of Maja Fruit Peel Extract Inhibitor Solutions

A. Tannin Extraction from Maja Fruit Peel

Maja fruit peel powder will be extracted using 96% ethanol solvent and with a temperature in the extraction process with a temperature of 60°C. The extraction process is carried out by stirring and heating. The extract is separated from the precipitate by filtering to obtain a filtrate. The liquid filtrate is evaporated using a rotary evaporator to produce a concentrated extract.

B. Tannin Quality Testing

Tannin Qualitative Test on Maja Fruit Peel Extract was carried out using a spectrophotometer

3.4.3 Coupon Preparation

Coupon formed with a size of 1 x 1 cm. Then, it is sanded to clean and remove dirty parts and then washed with distilled water and it is clean, then dried.

3.4.4 Coupon Corrosion Test with Potentiodynamic Polarization Method

Corrosion testing was carried out using the potentiodynamic polarization (PDP) method. This method uses 3 electrode systems, namely Platinum (Pt), Ag – AgCl, and Stainless Steel respectively as auxiliary electrodes, standard electrodes, and working electrodes. The system is then connected to a potentiostat and software as a data processor. The input potential used is from -1 V to +1.5 V with a scan rate of 1 mV/s. Coupons (SS 304, SS 316, Carbon Steel) were soaked for approximately 15 minutes in a corrosion medium of seawater and 3.5% hydrochloric acid with various concentrations of tannin extract (0

ppm; 100 ppm; 200 ppm; 300 ppm; 400 ppm; 500 ppm). The obtained tafel polarization curve is then extrapolated, to obtain corrosion parameters in the form of corrosion current density (I_{cor}), corrosion potential (E_{cor}), cathodic tafel slope (β_k),

4 Results And Discussion

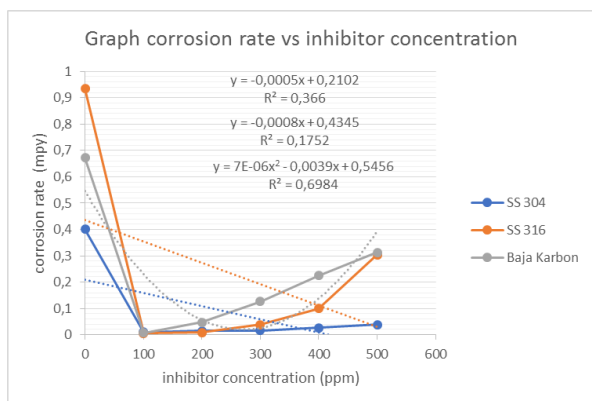


Fig 3. Graph of Corrosion Rate with Inhibitor Concentration

In Fig 3 it can be seen that the use of maja rind extract inhibitors to control the corrosion rate on SS 304 the best conditions were obtained at a concentration of 100 ppm with a decrease in the corrosion rate of 0.40128 mm/y. In SS 316 the best conditions were also obtained at a concentration of 100 ppm with a decrease in the corrosion rate of 0.93470 mm/y. The same thing happened to the Carbon Steel Plate the best conditions were obtained at a concentration of 100 ppm with a decrease in the corrosion rate of 0.6715 mm/y. This is because maja fruit skin contains a lot of tannin compounds so that it can form a thin layer that coats the entire surface of the metal. This layer can suppress metal oxidation reactions so that electron transfer can be inhibited [16].

The addition of inhibitors with a concentration of 200 ppm to 500 ppm has increased, because excessive inhibitors of maja fruit peel extract can make the layer on the metal surface thicker and bulge and then the layer breaks and causes the surface that is not covered to ionize so that it experiences corrosion. In addition, there are impurities in tannins that stick to metal surfaces so that they can accelerate corrosion.

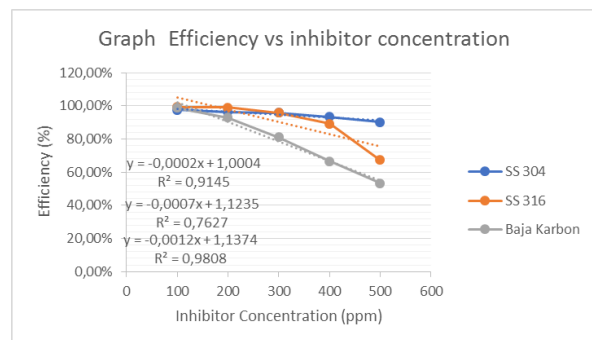


Fig 4. Graph of Efficiency with Inhibitor Concentration

In Fig 4. it can be seen that the use of maja peel inhibitors on SS 316 is more effective in suppressing the corrosion rate than SS 304 and Carbon Steel. This is because tannin compounds can form a thin layer on the surface of SS 316 more perfectly and cover the entire metal surface than SS 304, besides that SS 316 has a higher Cr (Chromium) content than 201 which has anti-corrosion properties and better strength. The composition of the SS 304 alloy is 0.05% C, 18.1% Cr, 8.3% Ni [25].

The addition of maja rind extract inhibitor in a 3.5% sodium chloride (NaCl) corrosive solution, the highest efficiency can reach 99.4% on SS 316 with a concentration of 100 ppm and on SS 304 it can achieve an efficiency of 97.6% at a concentration of 100 ppm and Carbon Steel can achieve an efficiency of 98.84% at a concentration of 100 ppm.

5 Conclusions and Recommendations

5.1 Conclusion

1. The best concentration in controlling the corrosion rate of SS 304 was obtained at 100 ppm with a corrosion rate of 0.00963 mpy, for SS 316 it was obtained at 100 ppm with a corrosion rate of 0.00521 mpy, while on steel plate it was obtained at 100 ppm with a corrosion rate of 0.00774 mpy.
2. The best inhibitor efficiency on SS 304 can reach 97.6% with the best concentration of 100 ppm, on SS 316 it can reach 99.4% with the best concentration of 100 ppm, and on steel plate it can reach 98.84% with the best concentration of 100 ppm.

5.2 Suggestion

1. We recommend that the metal plate must be sanded well so as to minimize the presence of rust and maximize the results
2. It is better if the research is carried out with more and different concentration variables
3. It is better to pay more attention to the cleanliness of the tools used in the manufacture of inhibitor solutions

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