Utilization of Natural Extracts as Corrosion Inhibitors in the Seawater Environment

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Abstract
Infrastructures in coastal area are mostly made of metal which is susceptible to corrosion due to direct contact with the seawater. The Seawater greatly affects the corrosion rate of metals because it contains chloride ions which can penetrate metal surface. The process of corrosion can be inhibited or slowed by decreasing the corrosion rate in one way, namely the addition of corrosion inhibitors derived from natural materials containing tannin compounds. This study proposed organic corrosion inhibitors which were derived from natural material extracts (coffee leaves and catappa leaves), the effect of time variations on the efficiency of organic inhibitors was investigated, and the efficiency of each inhibitor organic was compared. The corrosion rate with and without inhibitors was analysed by using the method of weight loss. The results showed that the corrosion rate can be reduced by adding the natural ingredients extract. The addition of 2% concentration coffee leaves extract resulted in the lowest corrosion rate with the addition of 0.00226 mmpy. The addition of catappa leaves extract concentration as much as 2% yield the lowest corrosion rate with the addition of 0.0012 mmpy. The highest efficiency of inhibition system was obtained by using 2% catappa leaves extract at 14 days soaking time at 69.23%, and the lowest by using 1% coffee leaves extract.

Keywords: inhibitor, natural extract, tannin, corrosion, sea water

1. Introduction
Corrosion is one of the causes of weathering in metals. Corrosion is a process that occurs naturally leading to a decrease in material quality through chemical or electrochemical reactions with the surrounding environment (Xhanari and Finsgar, 2016). In the mechanism, the metal will oxidize in a positive electrode which loses electrons and turns into positive ions (Chen et al., 2017). While on a negative electrode, there will be a reduction reaction and get electrons while forming negative ions. Positive and negative ions will join the electrolyte solution and produce hydroxides that are not soluble in water. The hydroxide formed is then oxidized with oxygen and water.

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \]
\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \]
\[ \text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \]
\[ 4\text{Fe(OH)}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 \]

Some environmental factors that can affect the corrosion process include (Haryono et al., 2010):

a. Temperature
The increase in temperature will cause an increase in the speed of the corrosion reaction. This effect occurs because of the higher temperature of the particles in action will increase so that it exceeds the magnitude of the activation energy price which results in the corrosion rate of metal also getting faster, and vice versa.

b. Fluid flow speed
Corrosion rate of metals tends to increase if the rate of fluid flow increases, this is because of the contact between the reactant and the metal will be greater. As a result,
there are more metal ions that will be released.

c. Corrosive material concentration
This is related to the pH of a solution. Acidic solutions are very corrosive to metals where metals in acidic media which will corrode more quickly because they are anodic reactions. While alkaline solutions can cause corrosion in the cathodic reaction always simultaneously with the anodic reaction.

d. Oxygen
The presence of oxygen in the air can come in contact with a moist metal surface causing greater corrosion.

e. Contact time
The action of inhibitor is expected to make metal resistance to corrosion greater. With the addition of inhibitor into the solution, it will lower the corrosion rate, so the working time of the inhibitor to protect the metal becomes longer. The ability of the inhibitor to protect the metal from corrosion will disappear or run out at a certain time, this is because the longer time, the inhibitor will be increasingly depleted by the solution.

The process of corrosion of metals cannot be stopped, but it can only be controlled or slowed down (Irianti and Khairat, 2013). One way to minimize the effects of material degradation is by the use of corrosion inhibitors. Corrosion inhibitors are chemicals that are added in small amounts to a corrosive environment to reduce the rate of corrosion between the surface and corrosive environment (Raja et al., 2016). Inhibitors work by coating the entire metal surface; forming a thin membrane to prevent the metal from being oxidized.

Generally, the inhibitors used are inorganic inhibitors, but these compounds are dangerous, expensive, toxic, and harmful for the environmental (Irianti and Khairat, 2013). Therefore, other alternative sources that come from organic materials are sought, which are later called organic inhibitors. Organic inhibitors can affect the corrosion rate of metals by injecting a small amount of concentration into a corrosive environment, which then being adsorbed chemically or physically on the surface, thus reducing the rate of corrosion effectively (Javidi et al., 2018). Corrosion inhibitors act in two steps, namely the transfer of molecules on the metal surface and the interaction of inhibitor functional groups with the metal surface. Important parameters considered for the use of inhibitors are the solubility of the inhibitor in the corrosive medium, adjustment of the inhibitor in the corrosive medium, stability, production costs and environmental efficiency of the inhibitor (Raja et al., 2016).

Organic inhibitors are made from plant extracts. This extract contains natural compounds such as tannin. Tannin is a complex compound of polyphenolic compounds that are non-toxic and biodegradable. It can be found on the skin and leaves of green plants (Nardeli et al., 2019). Hydroxyl groups in aromatic rings of tannin molecules can react with metals by donating electrons. The tannin molecules will be adsorbed on corroded metal surfaces and form a protective layer to protect from water molecules and inhibit the entry of other compounds that damage (Kaco et al., 2018).

The sources of tannins are coffee and catappa leaves. These two are chosen because of the abundance and the amount of tannin stored in the leaves. According to (Wulandari, 2014) the tannin content in coffee leaves is 3.12% and in catappa leaves, it can reach 7.23% based on the length of the extraction time (Pramudita et al., 2018).

Several study on the use of natural extracts as corrosion inhibitors have been reported. Pandan leaf extract as a corrosion inhibitor of SS-304 steel in H₂SO₄ solution obtained an inhibition efficiency of 89.06% (Kayadoe et al., 2015). In seawater medium, it has been reported by Irianty and Khairat (2013) that by using papaya leaf extract on AISI 4140 steel, the highest inhibitor efficiency of 21.59% in immersion for 36 days could be achieved. Pramudita et al. (2018) investigated the effect of tannins in catappa leaves extract to inhibit corrosion rates. The medium used was 1 M H₂SO₄. The research found that the corrosion rate increased significantly from 50 – 90 mmpy with increasing immersion time (i.e., 3, 6, and 9 hours). This means that H⁺ ions were so powerful against mild steel coated with inhibitor. Thus, in a relatively short period, the passive layer of the catappa leaves extract as an inhibitor could not completely protect the steel surface from corrosion.

In this study, the type of medium used was 1 M HCl. This is because HCl has a chloride component, which mainly causes seawater corrosion. In addition, the attack by H⁺ ions against the inhibitor were not as strong as in
the previous study, as a result, the inhibitor could work well, and the efficiency could also be investigated. Furthermore, the immersion time was also set longer (i.e., 7 – 35 days), so that it could precisely mimic the corrosive conditions in the seawater environment, which are mostly occurred slowly. For comparison with catappa leaves extract, coffee leaves extract was also used as an inhibitor.

Therefore, the purpose of this study was to examine the influence of organic inhibitors derived from coffee and catappa leaf extract in inhibiting corrosion rate occurred in metals. This study was also to investigate how organic inhibitors with different concentration can affect the corrosion rate of metals as well as to determine the efficiency ratio of each inhibitor.

2. Materials and Method

2.1. Materials

The materials used in this study were coffee leaves (derived from coffee plantations in Aceh Tengah), catappa leaves, AISI 4340 steel plates, and sea water. The seawater was taken from the coastal area of Banda Aceh with certain characteristics (Table 1). Additional materials include ethanol 96% (Merck, Germany), HCl 37% (Merck, Germany) and aqua dest.

Table 1. Characteristics of seawater (Ondara et al., 2020)

| Parameters         | Value      |
|--------------------|------------|
| Salinity           | 28‰       |
| pH                 | 8          |
| Temperature        | 29.8°C     |
| Dissolve oxygen    | 7.9 mg/L   |

2.2. Metal sample preparation

Metal samples (AISI 4340 steel plate) were prepared with 2 cm x 2 cm, and the initial corrosion product was removed from the metal surface. The plate was soaked in HCl solution for the pickling process and rinsed with distilled water and ethanol. The initial weight of metal samples was then measured.

2.3. Inhibitor extraction preparation

Initially, coffee leaves and catappa leaves were dried using indirect sunlight and oven at 40°C. Each of the drying process took 24 hours. After that, the leaves were pulverized smoothly using blender. The refined natural ingredients were extracted using ethanol solvent for 5 hours at temperature of 50°C while simultaneously being stirred. All the ingredients were then filtered. Finally, the filtrate was evaporated by the solvent until a concentrated extract was obtained.

2.4. Preparation of medium corrosion

The corrosion medium was prepared according to the number of samples. The medium and aerator were also prepared according to Figure 1.

2.5. Corrosion rate testing

A 100 mL seawater and the inhibitors with the concentration of 1% and 2% v/v (if necessary) were put into the glass. The metal samples were immersed with different time variations from 7, 14, 21, 28, to 35 days. The aerator was turned on to regulate air circulation in the seawater.

2.6. Analysis of corrosion rate

The metal samples that have been immersed are then dried and then weighed. After that, they were immersed back into the HCl solution for the pickling process until the mass of the metal sample was constant and weighed as the final weight. Measurement of corrosion rate can be carried out experimentally by weight-loss method using Eq. (1) (ASTM, 1999).

\[
CR = \frac{W \times K}{\rho \times A_s \times t}
\]  

Remark:
CR : corrosion rate (mmpy)
K : corrosion rate constant of the weight loss method
W : weightloss (initial – final) (gram)
A_s : sample area (cm²)
ρ : density (gram/cm³)
t : residence time (hours)

Corrosion rate depends on many constants selected. The corrosion rate constants that can be used to calculate the corrosion rate at various units according to ASTM (1999) can be seen in Table 2. The efficiency of the inhibitor is obtained by comparing the corrosion rate of with and without the inhibition system. However, the most important parameter in determining the efficiency of inhibitor is by the amount of inhibitor concentration used (Gartner et al., 2016).
Table 2. Corrosion rate constant value

| Corrosion rate unit used | Constant value (K) |
|-------------------------|--------------------|
| Mils per year (mpy)     | $3.45 \times 10^6$ |
| Inches per year (ipy)   | $3.45 \times 10^3$ |
| Inches per month (ipm)  | $2.87 \times 10^2$ |
| Millimetres per year (mm/y) | $8.76 \times 10^4$ |
| Micrometres per year (µm/y) | $8.76 \times 10^6$ |
| Picometres per second (pm/s) | $2.87 \times 10^8$ |
| Grams per square metre per hour (g/m²h) | $1.00 \times 10^4 \times D$ |
| Milligrams per square decimetre per day (mdd) | $2.40 \times 10^6 \times D$ |
| Micrograms per square metre per second (µg/m²s) | $2.78 \times 10^6 \times D$ |

The efficiency of inhibition is expressed in IE(%) (Yadav et al., 2016). Meanwhile, the metal corrosion inhibition can be determined using Eq. (2).

$$IE = \left( \frac{CR^0 - CR}{CR^0} \right) \times 100\%$$  \hspace{1cm} (2)

Remark:

IE : efficiency of inhibition (%)  
CR$^0$ : corrosion rate without inhibitors (mmpy)  
CR : corrosion rate with inhibitors (mmpy)

3. Result and Discussion

3.1. The Effect of Organic Inhibitors on Corrosion Rate

Weight loss was determined as it directly affected the corrosion rate, which was caused by corrosion products formed due to the longer contact time between metals and corrosive media. Typical corrosion products formed due to seawater immersion are commonly identified as iron hydroxide, iron oxide, iron chloride salts, and hydrated iron oxide (Othman et al., 2018).

As seen in Figures 2 and 3, the corrosion rate behavior of metals for both inhibition and non-inhibition systems was slightly different. Still, overall the corrosion rate of the inhibition system was lower than non-inhibitory systems. In non-inhibition systems, it is seen that the rate of corrosion changed with the length of immersion time and is inversely proportional to the immersion time. This is because the corrosion rate of the metal was determined by the rate of diffusion of $H_2O/O_2$ into the metal surface that the longer the soak time the more layers of $Fe(OH)_3$ were formed to cover the metal surface. As a result, the
diffusion of $\text{H}_2\text{O}/\text{O}_2$ to the metal surface was blocked and caused the decreasing rate of corrosion more and more (Irianti and Khairat, 2013).

In the inhibition system with the coffee and catappa leaves extract, the corrosion rates at all soak periods (7, 14, 21, 28, and 35 days) were lower compared to non-inhibitory samples, that the highest corrosion rate was obtained at seven days of immersion and the lowest time of soaking was at 35 days. However, the addition of inhibitors by using the catappa leaf extract had a lower corrosion rate than the coffee leaf extract.

![Figure 3. Correlation between corrosion rate and immersion time on the addition of coffee leaf extract inhibitors and catappa leaf extract with a concentration of 2%](image).

An inhibition system can inhibit the corrosion rate of metals as it contains tannin compounds in the extract. Tannin compounds can form complex compounds and bind metal ions complex compounds produced from tannins. In this case, the metal ions will then coat the metal from direct contact with corrosive solutions, and thus the corrosion rate will decrease (Komalasari et al., 2018). However, the catappa leaf extract were better in inhibiting the corrosion rate than the coffee leaf extract as the tannin content in the catappa leaves was more than that of the coffee leaf extract.

3.2. The Effect of Organic Inhibitor Concentration on Corrosion Rate

The increased inhibitor concentration of the leaf extract added to the seawater media decreased the corrosion rate as shown in Figure 4. This was due to the greater content of tannin compounds at high inhibitor concentrations. In this case, the role of complete compounds from tannins was as adsorbent on the metal surface that formed a protective membrane. These membranes play an important role to inhibit the rate of corrosion in the inhibition system (Pramudita et al., 2018).

The functional group that plays a role in the interaction between tannin molecules and the surface of the iron forming a protective membrane is the hydroxyl group. Hydroxyl groups on tannin surfaces can form covalent bonds with ferrous metals. This is supported by the more tannins adsorbed, the greater the inhibitory power and the lower the corrosion rate.

![Figure 4. Correlation rate of corrosion to the addition of coffee leaf extract inhibitors and catappa leaves with a concentration of 1% and 2% at the lowest corrosion rate obtained](image).

3.3. Comparison of Inhibitor Organic Efficiency

There was little difference in inhibitor efficiency behavior for the inhibition system with coffee and catappa leaf extract. However, the overall inhibitor efficiency for the inhibition system of coffee leaf extract was lower than the inhibition system of catappa leaf extract, as in Figures 5 and 6.

The efficiency of inhibitors for inhibition samples using coffee leaf extract at all soak periods (7, 14, 21, 28, 35 days) decreased even though the decrease was not linear. This was also seen on the inhibition samples using catappa leaf extract at all soak periods (7, 14, 21, 28, 35 days), which also experienced a decline even though it was not linear. This is related to the optimum time usage of the inhibitor, as the inhibitor can be attacked at any time by a solution. Thus, it can be said that the length of a soak can affect the efficiency of an inhibitor.
For the inhibition system at all soak periods (7, 14, 21, 28, and 35 days), the efficiency of the samples using catappa leaf extract was higher compared to the inhibition sample using coffee leaf extract. Therefore, it can be highlighted that the catappa leaf extract inhibitor works better than coffee leaf extract inhibitors. This relates to the content of tannin compounds that exist in extracts of these natural ingredients.

4. Conclusion

The addition of inhibitors from coffee and ketapang leaf extracts can constrain the corrosion rate. It is proven that in the inhibition system, the corrosion rate is lower than the corrosion rate in the non-inhabited system. The corrosion rate with an inhibitor concentration of 2% is better in terms of reducing the corrosion rate when compared to a concentration of 1%, this applies to the addition of catappa leaf extract or coffee leaves. In the analysis using the weight loss method, the smallest corrosion rate was obtained in the addition of 2% catappa leaf extract at the immersion time of 35 days, which was 0.0012 mmpy. This is because at high concentrations, a lot of tannin content in the inhibitor is added so that it is more optimal to coat metal samples. The inhibitor efficiency of catappa leaf extract is higher than in coffee leaf extract. This is because the content of tannin compounds in ketapang leaf extract is higher than in coffee leaf extract.

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