INTRODUCTION

Steel is a supporting material with a huge role in the maritime field. One of them is a raw material for shipbuilding. Low-carbon steel that is often used in ship construction is low-carbon steel A36. One of the causes of the decrease in the use value of a metal is the corrosion of the metal material. In operation, the ship sails over seawater which is a highly corrosive environment. Previous studies show that approximately 90% of ship damage, especially in the hull, is caused by corrosion [1]. The value of losses due to corrosion in Indonesia is estimated at $2 billion per year [2].

The process of corrosion on metal cannot be stopped and can only be slowed down. Therefore, corrosion protection continues to be carried out to obtain a suitable corrosion protection method. The use of corrosion inhibitors is the best method of preventing damage or degradation of metal surfaces from corrosive media. Corrosion inhibitors are divided into two, namely, inorganic and organic inhibitors. The basic materials of inorganic inhibitors include chromates, nitrates, silicates, and phosphates. These compounds are beneficial in anti-corrosion coating applications but have a significant drawback, which is toxic and dangerous to human and animal life. Meanwhile, organic inhibitors are environmentally friendly because they come from plant roots, stems, leaves, fruit, and other parts and contain chemicals such as tannins and flavonoids [3]. Organic inhibitors have the advantage of being readily biodegradable, safe, easy to obtain, and cheap because they come from natural ingredients.

In general, organic inhibitors contain antioxidant compounds. Antioxidant compounds can delay, slow down and prevent the oxidation process. Therefore, these compounds are assumed to inhibit the corrosion rate [4]. One of the efficacious plants as a natural antioxidant is cherry leaves (Muntingia calabura L.). Kersen leaves contain alkaloids, flavonoids, and tannins, which can be used as antioxidants [5]. High antioxidant activity is produced by cherry leaves which are thought to have the potential as a strong antioxidant with an IC value of 18.214 ppm [6].

An effective organic corrosion inhibitor must contain heteroatoms with lone pairs of electrons, and within their structural framework are electrons [7]. Cherry leaves contain elements of nitrogen, phosphorus, potassium, magnesium, and organic compounds such as tannins, alkaloids, and flavonoids. These compounds contain heteroatoms and conjugated double bonds as the main adsorption centers of corrosion inhibitors [8].

To find out the efficiency of the corrosion inhibitor of cherry leaf extract on A36 steel, it can be done by comparing the corrosion rate of the metal without the inhibitor with that of the metal given the cherry leaf extract inhibitor. Therefore, using cherry leaf extract as a corrosion inhibitor is an important matter that needs to be developed and further investigated by varying concentrations to produce an efficient method for inhibiting the corrosion rate of A36 steel.

RESEARCH METHODS

Preparation of Cherry Leaf Extract

Fresh cherry leaves are washed thoroughly...
with running water and then drained. After that, the leaves are dried so that colored leaves are brown and are easy to destroy. Dried cherry leaves are then crushed using a blender to obtain cherry leaf powder. 1000 gr of cherry leaf powder is macerated with 4 liters of 96% ethanol. The maceration process was carried out for three days. After three days, the cherry leaf extract solution was filtered using filter paper. Kersen leaf ethanol extract filtrate was concentrated using a tool rotary evaporator to obtain a thick extract of cherry leaves.

**Phytochemical Testing**

The alkaloid test was carried out by taking 2 mL of extracted cherry leaf samples into a test tube and adding five drops of dragendorff reagent. The color change and the formation of an orange precipitate are positive for alkaloids [9].

The flavonoid test was carried out by taking 2 mL of sample extract and adding 0.1 gram of Mg powder and five drops of concentrated HCl. A change in color from yellow to orange indicates a positive for flavonoids [9]. The tannin test was carried out by taking 2 mL of sample extract, then adding a few drops of FeCl₃ 1%. A change in color to dark blue or green-black indicates a positive tannin [9].

The Saponin test is carried out by taking 2 mL of sample extract into a test tube, then adding distilled water and shaking vigorously for 30 seconds; if stable, foam is formed between 1-10 cm, indicating positive saponins [10].

**Steel Sample Preparation**

The sample used is A36 steel. A steel sample with dimensions of 30x30x6 mm, the top of the steel plate was perforated using a drill so it could be hung during the immersion process. The steel plate was then smoothed with 80, 200, 400, 600, 800, and 1000 grid sandpaper until glossy to remove the oxide layer on the sample's surface. After all the shiny samples were washed using distilled water and dried, the samples were weighed using a digital balance to determine the initial weight. Microstructure testing was carried out using an optical microscope.

![Figure 1. Dimensions of the Test Specimen](image)

**Preparation of Inhibitor Solution**

The cherry leaf extract solution is diluted with the solution distilled water so that the desired concentration is obtained by using the following equation:

\[
M_1 \times V_1 = M_2 \times V_2
\]

Information:
- **M1**: Concentration of stock solution which is 100% (ppm)
- **M2**: Desired concentration of solution (ppm)
- **V1**: Stock volume to be dissolved (ml)
- **V2**: Volume of treatment solution (ml)
- **M1** x **V1** = **M2** x **V2

**Preparation of Corrosion Solutions**

The solution used for corrosive media is seawater. In the immersion test (immersion test) laboratory scale, the volume of the immersion solution can be calculated using a formula based on ASTM G31-72 standards.

\[
\text{Solution volume} = (0.20 \text{ to } 0.40) \times \text{surface area.}
\]

Surface area = 2 × (p×l + p×t + b×t) – (2µr²) + (tx2µr).

The minimum volume of immersion solution which will be used is:

\[
\text{Solution Volume} = 0.20 \times (2\times(30\times30+ 30\times6 + 30\times6) – (2\times3.14\times2²) + (6\times3.14\times2)) = 0.20 \times 2419.52 \text{ mm}² = 483.90 \text{ ml}
\]

Information:
- **P** = specimen length (mm)
- **l** = specimen width (mm)
- **T** = specimen thickness (mm)
- **R** = specimen radius (mm)

Based on the existing formula and the dimensions of the specimens that have been measured previously, the total volume of the solution used in the test can be calculated. From the calculations that have been done, it can be obtained that the volume of the solution used to soak the specimens with dimensions of 30 mm x 30 mm x 6 mm is 485 ml.

**Immersion of Steel in Corrosive Media Without Inhibitor Addition**

Five test containers are provided, labeled, and filled with seawater. Then the prepared steel plate is put into the container and soaked for seven days. After seven days, the samples were removed and cleaned of traces of corrosion by washing with distilled water and drying. After that, the steel sample was weighed with a digital balance to determine the final weight of the sample.

**Steel Immersion in Corrosive Media With Addition Of Inhibitors**

Twenty-five containers for immersion have been labeled and filled with seawater. Fifty ml of inhibitor was added to each container with 100, 200, 300, 400, and 500 ppm concentrations. Furthermore,
the steel plates that have been prepared are put into each container simultaneously and soaked for seven days to determine the final weight. After soaking for seven days, the steel samples were removed. Furthermore, the sample is washed with distilled water to clean the corrosion that sticks and then dried.

**Testing Weight Loss**

Weight loss was tested by immersing 30 specimens with inhibitors and five specimens without inhibitors in a seawater immersion solution for later comparison of results. Soaking is done for seven days. Before and after immersion, the initial and final mass of the specimen was weighed. Then after the immersion test, the corrosion rate calculation is carried out.

**Microstructure Analysis**

Microstructural analysis of a study using an optical microscope. Observation of the sample surface was carried out twice, namely before and after sample immersion.

**RESULTS AND DISCUSSION**

**Inhibitor Extraction Results**

The organic inhibitor used was made from cherry leaf extract (*Muntingia calabura* L.), which is added to a corrosive solution, namely sea water, to reduce the corrosion rate of A36 steel. The extraction process is carried out by the maceration method. This method is used to extract compounds that are less resistant to heat. The maceration process is very beneficial in the isolation of natural compounds because apart from being cheap and easy to do, immersing plant samples will cause the breakdown of the cell wall and membrane due to the pressure difference between inside and outside the cell, so the secondary metabolites present in the cytoplasm will dissolve in the solvent [11].

A total of 1000 grams of cherry leaf powder was added to 4 liters of 96% ethanol solvent and soaked for three days. The cherry leaf extract solution is then filtered using filter paper. The resulting filtrate was then concentrated with a rotary evaporator to eliminate the ethanol solution that was still present in the filtrate so that a concentrated extract from cherry leaves was obtained. The resulting extract has a greenish-black color. It shows that cherry leaf extract has a tannin content, a type of antioxidant [12]. Inhibitors will still be able to inhibit the corrosion rate as long as the layer formed is still there, but if the layer is gone, then the corrosion process can occur. As much as 100 ml of cherry leaf extract was produced, then 1 L of 500 ppm inhibitor mother liquor was made by mixing 0.5 ml of cherry leaf extract into 999.5 ml of distilled water. The 500 ppm mother liquor was then diluted into 50 ml of 100, 200, 300, and 400 ppm inhibitor solutions.

**Phytochemical Test Results**

The phytochemical test of cherry leaf extract aims to determine the presence of secondary metabolite compounds in the extract that play a role in the inhibition process. Phytochemical screening was carried out qualitatively using phytochemical reagents. The following are the results of phytochemical testing.

<table>
<thead>
<tr>
<th>Active compound</th>
<th>Positive test result</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaloids</td>
<td>An orange precipitate formed</td>
<td>-</td>
</tr>
<tr>
<td>Flavonoids</td>
<td>Color change from orange to red</td>
<td>++</td>
</tr>
<tr>
<td>Tannins</td>
<td>Discoloration to green or blue-black</td>
<td>+++</td>
</tr>
<tr>
<td>Saponins</td>
<td>Stable foam is formed (1-10 cm high foam for 30 seconds)</td>
<td>-</td>
</tr>
</tbody>
</table>

The results of phytochemical tests on the content of secondary metabolites in cherry leaf extract were positive for flavonoids and tannins. The presence of these compounds indicates that cherry leaf extract has the potential to inhibit corrosion rates. Tannins can increase the formation of films on metal surfaces so that they can help the corrosion inhibition process. The inhibition of tannins is associated with forming a passive layer of tannin on the metal surface. Tannins containing hydroxyl groups can react with iron ions to form Fe-tannate, forming an insoluble complex layer that will become a barrier to water or corrosive solutions for direct contact with ferrous metals [13].
This layer protects the steel so that the corrosion rate will decrease. Besides that, there are derivatives of flavonoid phenol that have antioxidant activity. Antioxidant compounds can delay, restrain and prevent the oxidation process.

**Influence Inhibitor Concentration Against Corrosion Rate**

This analysis is based on the weight reduction in the sample when it is immersed. The corrosion rate of A36 steel specimens is necessary to know the weight of the steel lost due to corrosion. The initial weight is weighed at the preparation stage of the A36 steel specimen, and the final weight is weighed after the corrosion test ends. The weight of the steel specimen was measured using a digital balance. The lost weight can be calculated from the difference between the initial and final weights of the A36 steel specimen.

Calculations are performed using the following equation (ASTM G1-03)

\[
CR = \frac{KW}{3.45 \times 10^6 \cdot A \cdot T \cdot D}
\]

\[
(1)
\]

Information:

- CR = Corrosion rate (mpy)
- W = weight Lost (grams)
- K = Constant (3.45 x 10^6)
- A = Luas Area (cm^2)
- T = Immersion time (hours)
- D = Density (grams/cm^3)

The loss of sample weight is affected by immersion time and the addition of inhibitors to the solution. Samples soaked without inhibitors will lose more weight than samples soaked with inhibitors added. The lost weight data that has been obtained previously is used in the calculation of the corrosion rate. The corrosion rate can be calculated based on equation (1).

Results in Figure 2 show the effect of the addition of inhibitor concentration on the corrosion rate and inhibition efficiency. The greater the concentration added, the smaller the corrosion rate; this indicates an inverse relationship between the concentration and the resulting corrosion rate. It is due to the high concentration of inhibitors resulting in the frequency of interactions between the active sites of the molecule and the more surface area of the specimen, thus forming a stable passive layer which results in a greater surface area of steel being covered and blocking the attack of corrosive solutions [14]. It shows that cherry leaf extract can be used as a corrosion inhibitor on steel. The reduced value of the sample corrosion rate was due to the content of antioxidant compounds in cherry leaves in the form of tannins which can form Fe-tannate complex compounds with an iron surface, as seen in Figure 3[15-16].

The mechanism of corrosion inhibition by Fe-tannate complex compounds can be seen in Figure 3[15]. Tannic acid can form complexes with iron attached to the surface. In the process of dissolving iron carbon anode, oxidation of Fe to Fe occurs. Then, the oxidation of Fe into Fe ions by oxygen. Fe is reduced to Fe ions through contact with ferrous metal in the pores resulting in discoloration. Tannic acid acts on available iron ions in three ways. First, tannins can form complex compounds with Fe ions to ferro-tannate, easily oxidized to ferric-tannate in the presence of oxygen. Second, tannins can react directly with Fe ions from ferries. Third, because of the ability of the reducing properties of tannins, Fe ions can be reduced to Fe ions [13].

This Fe-tannate complex compound will be a
The highest corrosion rate was found in samples without the addition of inhibitors, reaching 0.1254 mmpy. Meanwhile, the lowest corrosion rate was the addition of a 500 ppm inhibitor, namely 0.0767 mmpy. Corrosion rates at inhibitor concentrations of 0, 100, 200, 300, 400, and 500 ppm in a row are, namely, 0.1254 mmpy, 0.1097 mmpy, 0.1052 mmpy, 0.0935 mmpy, 0.0880 mpy and 0.0767 mpy. Corrosion resistance for steel is said to be very good if the corrosion rate is in the range of 0.02 - 0.1 mmpy. The results of this study can be concluded that the A36 steel sample is relatively resistant to corrosion attack in a seawater environment. The higher the inhibitor concentration, the more compounds are contained in the extract, and the more these compounds will be absorbed on the steel surface absorbed. The compounds in the extract on the steel are caused by the process of filling electrons from the extract compounds in the empty Fe orbitals on the steel plate so that Fe is more stable with the filling of electrons which is not easy to oxidize and makes the steel surface layered as well as being blocked against attack by aggressive ions and H molecules H₂O which can corrode. The effect of inhibitor concentration on the corrosion rate is shown in Figure 2.

From the corrosion rate obtained in Figure 5, the inhibition efficiency is obtained. Inhibition efficiency data is obtained from the percentage difference in corrosion rate according to equation (1)

\[
\text{Inhibition Efficiency} = \left( \frac{C_{\text{control}} - C_{\text{inhibited}}}{C_{\text{control}}} \right) \times 100
\]

where \(C_{\text{control}}\) is the corrosion rate of the control sample without inhibitors and \(C_{\text{inhibited}}\) is the corrosion rate of the sample with inhibitors. In this study, the inhibitor efficiency data is obtained from the percentage difference in corrosion rate. The corrosion rate is decreasing, and the inhibition efficiency is obtained. Thus, samples with inhibition efficiency of 38.83% with an inhibitor concentration of 500 ppm within seven days of immersion. And the lowest efficiency is 12.54% at 100 ppm inhibitor concentration. The increase in the efficiency value on the graph is in line with the decrease in the corrosion rate, as seen in Figure 5: the chart shows that the efficiency will increase with the increasing concentration of inhibitors in the immersion solution.

Results of Observation of Sample Microstructure

Microstructural observations were carried out to observe the microstructure of the steel surface at each variation in the concentration of cherry leaf extract before and after immersion. Figure 6 (a) shows a micro photo of the A36 steel surface before immersion.

In Figure 6 (a), No corrosion has formed on the surface of the steel. In the photo, you can see dark lines, which are the result of less fine sanding. Figures 6(b) to 6(g) show the steel's condition after immersion. The comparison of steel after immersion in solutions without inhibitors and with the addition of inhibitors with concentrations of 0, 100, 200, 300, 400, and 500 ppm can be seen. More corrosion products are formed in steel by immersion without inhibitors, Whereas samples with the addition of 500 ppm inhibitors had fewer corrosion products, and their surfaces looked smoother. Thus, samples immersed in solutions with lower inhibitor concentrations will have a rough surface due to more corrosion products than those with higher inhibitor concentrations.

The sample shows brown holes, which are corrosion products. Corrosion holes formed decreased with increasing inhibitor concentrations used. Inhibitors include a layer on the sample that is useful for inhibiting the corrosion rate by blocking the corrosive solution from making direct contact with the sample, thereby inhibiting the corrosion rate. It follows previous studies, which stated that there were changes in the surface morphology of the steel without and with the addition of inhibitors. The surface morphology becomes more even with increasing inhibitor concentration with increased adsorption so that it covers the surface [17-18].

Based on observations on the sample's surface, the type of corrosion that occurs on the sample is pitting corrosion. Pitting corrosion is a form of corrosion attack resulting in metal holes. The cause of this corrosion formation is the presence of chloride ions in the seawater immersion solution. The adsorbed chloride ions will react with metal ions in the film layer, producing holes.
Gambar 6. (a). The surface of A36 40x Steel Specimen No Corrosion, (b) Surface of A36 Steel Specimen 40x Concentration 0 ppm, (c) Surface of A36 Steel Specimen 40x Concentration 100 ppm, (d) Surface of A36 Steel Specimen 40x Concentration 200 ppm, (e) Surface of A36 Steel Specimen 40x Concentration 300 ppm, (f) Surface of A36 Steel Specimen 40x Concentration 400 ppm, (g) Microstructure of steel after immersion in 500 ppm concentration

CONCLUSION

Organic inhibitors from cherry leaf extract (*Muntingia calabura* L) can reduce the corrosion rate of A36 steel to 0.077 mpy with an efficiency value of up to 38.83% with the addition of 500 ppm inhibitor concentration in cherry leaf solution immersion. The organic inhibitors of cherry leaf extract can be used as an antifouling paint material for corrosion resistance which is applied to A36 steel plate material for ship hulls.

REFERENCES


