The effect of concentration and temperature on the activities of kenikir (cosmos caudatus) leaf extract as iron corrosion inhibitor in electrolyte solution of NaCl

T Sudiarti*, Y Yulianti and A Supriadin
Chemistry Department, Universitas Islam Negeri Sunan Gunung Djati Bandung, Bandung, Indonesia

*etty.sudiarti@uinsgd.ac.id

Abstract. Ethyl acetate extracts from kenikir leaves contain flavanoid, alkaloids and tannins compounds. This compound can be used as a corrosion inhibitor because it contains nitrogen and oxygen atoms with a pair of free electrons so that it allows adsorbed strongly on the surface of the iron and increases the activity of corrosion inhibition. The inhibitory activity was analyzed by wheel test method or measurement of weight loss in NaCl 1 % medium with variations in concentration, temperature and electron microscopy (SEM) analysis. The inhibitory activity of kenikir leaf extract increases with increasing concentration of inhibitor. The optimum inhibition efficiency of was obtained at a concentration of 32 ppm with an inhibition efficiency of 86.84%. An increase in temperature from 25-55 °C causes decreased inhibitory activity and achieves optimum inhibition efficiency at 25°C. Kenikir leaf extract has adsorption properties that correspond to the Langmuir adsorption isotherm with free energy of ΔGads of -14.98 KJ / mol. The results of the surface analysis by Scanning Electron Microscopy (SEM) showed that the kenikir leaf extract could inhibit corrosion rates with iron surfaces that had fewer pores than without inhibitors.

1. Introduction
Corrosion is a redox reaction between a metal and various substances in its environment that produce compounds that can reduce the quality of a material. The metal contact with its environment can cause the deterioration of surface properties, morphology changes and color transformation [1]. Corrosion can occur in metal materials used in various industries, including the mining industry. In the mining industry, iron is used as a pipeline for petroleum. The impact arising in the event of corrosion on the inside of the pipe in the mining industry is a serious metal degradation process that requires very burdensome maintenance costs [2]. One of the most commonly used methods to control and reduce corrosion is by corrosion inhibitors [3]. The effective, easy and inexpensive way to control and prevent corrosion on the inside of a pipe is to use a corrosion inhibitor [2].

Corrosion inhibitors are chemical compounds that are added in small amounts to the media to slow the corrosion. Generally, corrosion inhibitors come from synthetic chemicals which are dangerous chemicals, the price is relatively expensive and not environmentally friendly. To overcome this, organic inhibitors can be used because they are easily degraded so they are environmentally friendly. Organic inhibitors can be adsorbed on the metal surface and form a thin layer that can reduce ionic transfer from metal to medium and reverse [4]. One alternative of the organic inhibitor is to use inhibitors derived...
from extracts of natural materials, especially compounds containing hetero atoms such as nitrogen, sulfur, phosphorus and/or oxygen atoms [5]. The atoms have free electron pairs that can be adsorbed strongly on the iron surface. One alternative natural inhibitor that can be used is kenikir leaf (Cosmos caudatus) which is abundant in Indonesia because it is easy to grow anywhere. Extracts of kenikir leaf (Cosmos caudatus) contain alkaloids, flavonoids and tannins compounds, which contain nitrogen and oxygen atoms that have free electron pairs so that they can function as inhibitors.

The purpose of this study is to determine the corrosion inhibition activity of kenikir leaf extract (Cosmos caudatus) on iron in 1% NaCl solution which is an artificial condition in the mining industry. In the extraction process ethyl acetate is used as a solvent to dissolve the active substances that are in the kenikir leaves, then characterization is done using phytochemical tests. In this study the inhibition test was based on the Wheel Test (weight loss) method by using variations in concentration and temperature to determine its effect on the effectiveness of inhibitors, and the morphology of iron before and after the addition of inhibitors was analyzed using SEM (Scanning electron microscopy) [6].

2. Methods

2.1. Materials
The materials used in this study are kenikir leaf, ethyl acetate, ferri chloride (FeCl3), magnesium (Mg), Chloride acid (HCl), Dragendorff reagent, distilled water, sodium chloride (NaCl) pa, iron metal, technical acetone, carbide silicon sandpaper.

2.2. Preparation of kenikir leaf sample
Kenikir leaf samples that have been separated from the stem are dried and then crushed using a blender to form powder.

2.3. Extraction of kenikir leaf sample
Weighed 500 grams of kenikir leaf powder put into a 1000 mL beaker, then added 375 mL of ethyl acetate. Maceration was carried out for 3 times 24 hours, every 24 hours the ethyl acetate extract was filtered and macerated again with new ethyl acetate solvents. The ethyl acetate extract of kenikir leaves obtained was evaporated by using a vacuum rotary evaporator (rotary vacuum evaporator) at a temperature of 30-40 ° C to form a thick extract of ethyl acetate.

2.4. Characterization of kenikir leaf extract (phytochemical test)

2.4.1. Tanin test. Test extract solution was added with 2-3 drops of 1% FeCl3 solution, positive results were shown with the formation of bluish black or green.

2.4.2. Flavonoid test. The test solution was added with a small amount of Mg powder, alcohol solution: HCl (1: 1) and amyl alcohol, positive samples were indicated by the formation of red, yellow or green.

2.4.3. Alkaloid test. Samples are added 1-2 drops of Dragenroff, positive alkaloids are present if they are orange.

2.5. Preparation of inhibitor (kenikir leaf extract) solution
The thick extract of kenikir leaves was weighed in a watch glass, then put in a 250 mL beaker, dissolved with ethyl acetate up to 100 mL, then stirred until homogeneous. Pipetted then diluted to 8 ppm, 16 ppm, 24 ppm, and 32 ppm with 1% NaCl solution using a measuring flask.

2.6. Preparation of NaCl 1% solution
1% NaCl electrolyte solution is made by weighing 10 grams of NaCl solid and then dissolved in a beaker and diluted with distilled water in a 1 liter measuring flask up to the mark.
2.7. Preparation of iron sample
The iron surface is cleaned with silicon carbide sandpaper, cleaned with water and acetone, then made to a diameter that matches the tool set, weighed and then bound with mattress threads.

2.8. Measurement of corrosion rate by wheel test method and determination of inhibition efficiency (EI)
Test solutions with variations in concentration that have been made are put into vial bottles. Then the iron metal is immersed in the test solution, covered and allowed to stand for 45 hours. After 45 hours the metal was removed, cleaned, dried and weighed. The treatment was repeated with the effect of temperature variations at 25, 35, 45 and 55 ° C. Then the corrosion rate value is calculated using the following formula [7]:

\[ R = \frac{k \times \Delta w}{D \times A \times t} \]

(1)

Where respectively R, \( \Delta w \), D, A, t, k were corrosion rate (mm / year), lost weight (gram), density (g / mm³), section area (mm²), Immersion time (year), and constant (8.76 x 10⁴).

Then the efficiency of inhibitors can be determined using the following formula [8]:

\[ \% EI = \frac{CR_o - CR_i}{CR_o} \times 100 \]

(2)

Where respectively \% EI, CRo, CRi were inhibition efficiency, corrosion rate without inhibitor and corrosion rate with inhibitor.

2.9. Surface analysis by SEM
Test solution with a concentration of 32 ppm that has been made is inserted into a vial bottle. Then the iron metal is immersed in the test solution, covered and allowed to stand for 45 hours at 25 ° C. Then the metal metal is removed, cleaned and dried. Then a Scanning electron microscopy (SEM) analysis was performed.

3. Results and discussion

3.1. Characterization of kenikir leaf extract (Phytochemical Test)
This phytochemical test was carried out to determine the content of active compounds found in kenikir leaves, such as flavonoids, alkaloids and tannins. Based on the results of the flavonoid test, the ethyl acetate extract sample has a color change from green to orange, which indicates that it positively contains flavonoids. Tannin testing on kenikir leaf extract showed positive results, in the presence of blackish green color. Tannins in kenikir leaf extract are included in condensed tannins, because they change color to blackish green. Alkaloid testing on kenikir leaf extract showed positive results. Kenikir leaves give rise to an orange-red precipitate with Dragendorff reagents, these deposits are potassium alkaloids [9].

3.2. Effect of inhibitor concentration (kenikir leaf extract) to inhibition efficiency
Based on Figure 1, the effect of ethyl acetate extract inhibitor concentration from kenikir leaves can be seen in the corrosive NaCl 1% medium to the value of inhibitor efficiency. The efficiency of the inhibitors increases with increasing concentration of inhibitors and reaches optimum at 32 ppm inhibitor concentration with inhibition efficiency of 86.84%. The efficiency value is inversely proportional to the corrosion rate. This is due to the inhibitors mixed in the corrosive medium being able to protect the sample by forming a protective layer on the surface of the iron sample. Corrosion rate decreases with increasing concentration of inhibitors to an optimum limit, henceforth it increases again due to desorption.
3.3. Effect of temperature to inhibition efficiency

As shown in Figure 2, the inhibition efficiency decreases with increasing temperature. This shows the occurrence of the process of partial desorption of inhibitors on metal surfaces which is reinforced by observing the increased corrosion rate. The high efficiency value is at 25°C. The relationship of inhibition efficiency is inversely proportional to temperature, the more the temperature increases, the lower the value of the inhibition efficiency so that the corrosion rate increases [10]. When the temperature rises, the ions in the solution will move more freely so that a broad impact on the attack on the surface of the iron.

3.4. Adsorption isotherm

It can be seen in Figure 3 that the process of adsorption inhibitors on the iron surface produces a linear plot on the Langmuir adsorption isotherm curve. This proves that the regression results obtained follow the mechanism of the Langmuir adsorption isotherm. The Langmuir isotherm is based on the assumption that each adsorption site is equivalent, and the ability of particles to bind to a location does not depend on whether or not a place is close together.

From the linear equation, the K and ads Gads values involved in the adsorption process can be produced. The K value of the Langmuir equation is 7.6045 for ethyl acetate extract. A large K value indicates a quantitative equilibrium indicating the amount of kenikir leaf extract adsorbed on the iron surface so that the % EI value increases. Meanwhile, the value of ΔGads produced through the Langmuir equation in ethyl acetate extract was -14.98 kJ / mol. The value of ΔGads shows that the adsorption of kenikir leaf extract on iron is spontaneous. Based on the ΔGads value generated from the Langmuir equation, it can be concluded that the reaction of kenikir leaf extract extraction on iron is physisorption. That is because the value of ΔGads produced below -40 kJ / mol [11].
3.5. Surface analysis by SEM

Surface analysis by SEM (Scanning electron microscopy) can be used to assess the inhibitory effect of an inhibitor [12]. In Figure 4 the results of surface analysis with SEM shows that the surface of the iron in the electrolyte solution in the absence of an inhibitor formed defects or damage to the pores of the iron but with the presence of kenikir extract inhibitors formed a thin layer on the iron surface that protects the iron from corrosion. This proves that kenikir leaf extract can be said to be a barrier to the occurrence of corrosion (inhibitor), because it looks a thin layer that can reduce the rate of corrosion.

4. Conclusion

The inhibitory activity of kenikir leaf extract increases with increasing concentration of inhibitor. The optimum inhibition efficiency of was obtained at a concentration of 32 ppm with an inhibition efficiency of 86.84%. An increase in temperature from 25-55°C causes decreased inhibitory activity and achieves optimum inhibition efficiency at 25°C. Kenikir leaf extract has adsorption properties that correspond to the Langmuir adsorption isotherm with free energy of ΔGads of -14.98 KJ / mol. The results of the surface analysis by Scanning Electron Microscopy (SEM) showed that the kenikir leaf extract could inhibit corrosion rates with iron surfaces that had fewer pores than without inhibitors.

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