Development of green vapour corrosion inhibitor

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Abstract. Corrosion control using inhibitor is an effective method to protect carbon steel from corrosion. Due to environmental toxicity of chemical inorganic corrosion inhibitors (synthetic), green inhibitors are potentially to develop. In atmospheric conditions, green vapour corrosion inhibitors are the best solutions to replace the uses of inorganic corrosion inhibitors. This research used chemical acid extraction from the key lime (citrus aurantiifolia) leaves and seeds. They are used as the main ingredients to produce this effective green corrosion inhibitor. The experiments investigated effects of corrosion inhibition on corrosion rate of low carbon steel in 3% NaCl solution using both fog salt chamber and electrochemical cell. Using salt fog chamber to represent atmospheric conditions, and corrosion rates are evaluated visually and calculated using weight loss methods. Corrosion rate on electrochemical cell were calculated using linear polarization resistance (LPR) methods. All of the experiments were set in natural conditions at pH 7. Using weight loss for three days exposure time, the efficiency of the inhibitor reached 82.39%.

1. Introduction
Metallic structures are prone to corrode in atmospheric conditions, especially in marine environments. They are exposed to corrosive elements such as water vapour, and rain which is contained NaCl particles. Corrosion will occur quickly for the metallic structures made of carbon steel. There will be severe forms of localized corrosion, erosion corrosion and uniform corrosion. These forms of corrosion occur when water is absorbed and collected in the local area of the structures. To prolong the service life, the protection system should be applied to provide a barrier of corrosive elements penetration. Currently, inhibitor is the preferred protection choice from corrosion damages [1-4]. Corrosion inhibitor which are widely used in industries are commonly in liquid forms. In the forms of liquid, inhibitor cannot effectively protect carbon steel corrosion because liquid inhibitor cannot reach dry location. Thus, it needs inhibitor which can evaporate called volatile corrosion inhibitor (VCI) to protect steel corrosion in dry location. There are various kind of evaporating corrosion protection inhibitors had been develop since 1950’s in the industrial of metal fields. VCI has been widely used for the protection of metal surfaces in a container. VCI often combined with other corrosion protection medium in a packaging of machined parts, joining fasteners and more. The wrapping of the packaging usually will be coated to protect the object inside it. The usage of VCI inhibitors mostly applied in confined spaces to protect the product for temporary only [5]. The application of VCI is to protect stored tools or metal made product inside bags, boxes, storage during transportation or protecting a newly arrived metal product. Effectiveness of corrosion inhibitors also depend on quantity. Low inhibitor quantity cannot protect effectively, hence promote corrosion process. While excessive quantity of inhibitor will affect production cost. The effectiveness of an inhibitor is shown by its
impact on reducing corrosion rate. Recent researchers have used various types of inhibitor such as organic inhibitor or un-organic depending on environmental conditions [6].

The Key Lime Plant

The Key lime (Citrus aurantiifolia) is a citrus hybrid of Citrus micrantha and Citrus nedica with a spherical shaped fruit with the diameter from 2.5cm to 5cm (1–2 in). The colour of the fruit is yellow when ripe but usually picked green commercially due to it have stronger sour taste. In addition, it is smaller and seedier, with a higher acidity, a stronger aroma, and a thinner rind, than the Persian lime (Citrus latifolia). In Malaysia it is commonly known as ‘Limau Nipis’ which is very popular amongst Malaysia’s foods and drinks. On the other hand, key lime also famous for its health benefits than only giving taste to foods. For instance, it is used to treat nausea, headache, fainting, malaria, and sore throat. Many studies had been carried out regarding to the ability or function of the key lime plan food and health benefits. For example the studies that had been carried out based on the benefits of key lime plant are in the field of antioxidants, where the juice and peel do demonstrate antioxidant properties. In the field of corrosion inhibition, acid extract from both leaves and seed show impressive properties that can reduce the corrosion rate of metal especially in mild steel [7-10].

2. Research methodology

2.1. Electrochemical Set-up

A typical schematic three-electrode set-up used in all electrochemical experiments is shown in figure 1. A low carbon steel was used as the working electrode. Glass cell was fitted with graphite electrodes as auxiliary electrode and Ag/AgCl as a reference electrode.

2.2. Specimen Preparation

The working electrodes were carbon steels. The cylindrical specimens have diameter of 12 mm and 10 mm thickness which is used to electrochemical test. Weight loss and salt fog chamber test were used samples as shown in figure 1. Before immersion, the specimen surfaces were polished successively with 240, 400 and 600 grit SiC paper, rinsed with methanol and degreased using acetone. The experiments were repeated at least twice in order to ensure reasonable reproducibility.

![Figure 1](image1.png)

(a) (b)

**Figure 1.** Sample for (a) electrochemical test 1 x 3 cm and (b) sample for salt fog chamber tests.

2.3. Green inhibitor preparation

Key Lime Leaves and Seeds were used of inhibitors. The key lime leaves are obtained free from the fruit or groceries sellers in the market. Big amount of leaves are managed to be collected which is approximately to 1kg of key lime leaves. Meanwhile, the key lime seeds are obtained from the Pekan. Both the leaves and the seeds have almost the same concentration of acid compared to the key lime fruit itself. 500 gr of both of the leaves and the seeds are let to be dried under the sun to reduce the moisture content for three to four days until it turns into light brownish colour and the leaves becomes brittle. For the extraction of the plant materials, 25 gr of the powdered dry leaves and seeds poured
into 500mL of 1M HCL in a beaker. The powder concentration in the mixture is 5\% of (wt/vol) in the HCl solution.

2.4. Cell Solutions

The experiments were performed in stagnant solutions condition. Schematic electrochemical test was presented in figure 2. The test pressure was 1 bar, the glass cell was filled with 1 liter of distilled water and 3\% wt NaCl which was stirred with magnetic stirrer. Temperature was set using a hot plate. The Linear Polarization Resistance (LPR) technique was used to measure the corrosion rate. The procedure is similar to ASTM Experimental test G 5-94 [13].

![Figure 2. Schematic of corrosion test cell.](image)

2.5. Salt Chamber Experiment

Since this project is mainly focus in producing vapour corrosion inhibitor, thus this salt chamber experiment plays an important role in providing a suitable condition to test the inhibitor solution in vapour form and it is carried out by using the ECO Instrument Salt Chamber machine as presented in figure 3. This salt chamber is set into 35\(^\circ\)C as the control temperature in the chamber, spray time is set to five minutes and the overall process time is set to one hour. Before starting, it is a must to sand and polish the mild steel metal plate to get rid of oxidants or other residuals on the surface. The testing equipment consists of a closed testing chamber, where a salt solution mainly is atomized by means of a nozzle. This produces a corrosive environment in the chamber so that parts exposed in it are attacked under this severe corroding atmosphere.

![Figure 3. Salt fog chamber for the corrosion resistance testing, ASTM B117.](image)
3. Results and Discussion

3.1. Potentiodynamic Polarization Measurement.

The measurement is carried out with 500 mL and 20% (v/v) of NaCl solution or known as Blank solution. Then it is followed by the adding and increasing the amount of the inhibitor from 5mL (1% v/v) and 7mL (1.4% v/v) in the NaCl solution. Every measurement is obtained by the plotting of Tafel graph is presented in table 1. As calculated, the key lime inhibitor’s efficiency increases as the concentration increases in the NaCl solution.

Table 1. The Icorr values from the Tafel plot

| Concentration, v/v % | Icorr, A/cm² | Efficiency |
|----------------------|-------------|------------|
| 0 (Blank)            | 0.00007     | -          |
| 1 (5mL)              | 0.00006     | 14.57      |
| 1.4 (7mL)            | 0.00003     | 57.14      |

Figure 4. Polarisation graph of green corrosion inhibitor on carbon steel.

From the polarisation graph (figure 4), it is shown that green corrosion inhibitor can improve corrosion potential. Using 7 ml of inhibitor, potential corrosion of carbon steel on NaCl solution increased by 2V. It means that tendency of corrosion to start will reduced. Green corrosion inhibitors also may give the protection for both anodic and cathodic process [12, 13]. They work as a mixed corrosion inhibitor and change polarity of the samples. Inhibitors form a passivation films which inhibits the anodic metal dissolution reaction and causes largest anodic shift of the corrosion potential. Besides, it is important that the concentration of the inhibitor should be high enough. This is because, if may affect the formation of the film if the concentration is low and the metal surface might not be fully covered with the anodic corrosion inhibitor and localized corrosion may take place [14].

3.2. Weight Loss

Based on the figure 5, container I salt solution had turned from colourless to brownish-red colour. This shows that corrosion of the mild steel does occurs in this container. The cause of the colour change of the NaCl solution is due to the metal oxides that are formed during the corrosion process. The mild steel turn in to dark silver colour which shows that, the surfaces do faces oxidation in the three weeks period time. The salt formation is in smaller size like grains and sticks onto the surface of the cuboid together with the metal oxides. On the other side container II, the solutions remains the same greenish colour as the beginning of the experiment. The metal surface remains shiny as the initial condition and
there is no presence of metal oxides on the surfaces too compared to the sample from container I. By using weight loss method, the average of corrosion rate of samples I was 2.8775 mm/year is higher compared to the corrosion rate of samples II which us just 0.5066 mm/year. This shows that samples I corrodes faster than samples II during the presence of salt. Thus, the green inhibitor from the key lime reduces or slows down the corrosion rate of mild steel in during the presence of salt. The inhibitor efficiency of this project in this experiment is 82.39% as calculated.

![Figure 5. Comparison samples after three weeks without inhibitor (container I) and with inhibitor (container II) after three days experiments (b).](image)

**Table 2. The weighing of samples after 3 weeks immersion time.**

| Weighing Term | Samples I (gr) | Samples II (gr) |
|---------------|----------------|-----------------|
| Term 1        | 10.1134        | 10.3681         |
| Term 2        | 10.1137        | 10.3682         |
| Term 3        | 10.1133        | 10.3684         |

3.3. Salt Fog Chamber Experiment

For the first test, the sanded and washed metal plate that is left for one hour in the salt chamber without the presence of the inhibitor. The metal plate surface shows the corrosion precipitation to be more vigorous compared to the experiment with the presence of the inhibitor. Visually proven that the inhibitor does show some inhabitancy to fight against corrosion that occurs on the mild steel plate surface there is not much difference (figure 6). VCI usually have low or significant vapour pressure which includes the effective of the inhibiting properties. Besides that VCI also provides protection against moisture in the air through its vaporization and cover fully the surface of the metal by forming a thin film of protective layer. In addition, it also neutralize the carbon dioxide which is acidic and shifts the Ph of the metal surface towards less corrosive and acidic value. In other words, when the VCI come into contact with the metal surface it condensed and hydrolysed by the moisture for the liberation of the protective ions. If the vapour pressure is too low, another volatile substance such as water vapour or urea can be used as carrier of the VCI. The volatility can also be enhanced by the use of host guest systems where the VCI are incorporated to a porous substrate. Then, the VCIs are transferred to the metal surface by diffusion through the gas room and are adsorbed directly on the metal or dissolved in a surface moisture layer and reduce the corrosion rate markedly [15].
The mechanism of a corrosion inhibitor acts by undergoing chemisorption process, in which it is a chemically adsorb by the metal surface through the combination of the inhibitor ions and the metallic ions on the metal surface (figure 6). This will form a thin layer of protective film as the corrosion protection of the metal surface. Moreover, the inhibitor also causes the formation of oxide protection film of the base metal. The inhibitor undergoes a reaction together with the corrosive component which is potential in the aqueous media and a complex product is formed [16].

4. Conclusions
It is proven that application of this vapour green anticorrosion using key lime is reliable to reduce corrosion process. It can be applied both on dry and wet conditions. The highest efficiency was obtained in wet conditions which was 82 %. In dry conditions, efficiency inhibitor seemed not contributed significantly. Mechanism of inhibitor to protect carbon steel may be related to chemisorption process, in which it is a chemically adsorb by the metal surface through the combination of the inhibitor ions and the metallic ions on the metal surface to form film formation.

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