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Pomelo peels extract as green corrosion inhibitor for mild steel in hydrochloric acid 1 m

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Abstract. The inhibiting action of pomelo *(Citrus maxima*) peels extract have been investigated as environment-friendly corrosion inhibitor of mild steel in hydrochloric acid 1 M using weight loss measurements method. The measurements were conducted at a various concentration of pomelo peels extract and immersion time. The effect of pomelo peels extract concentration and immersion time on the rate of corrosion and inhibition efficiency were investigated. The rate of corrosion was calculated by a weight loss of initial and after immersion of the samples. The mechanisms of corrosion inhibition were determined by adsorption mechanism of inhibitor. The results revealed that pomelo peels extract was an effective corrosion inhibitor for mild steel in hydrochloric acid 1 M solution. The rate of corrosion is decreasing with the increase of pomelo peels extract concentration. The inhibition efficiency was considered to increase with pomelo peels extract concentration to attain 92.2% at 1.6%. The mechanism of inhibition of corrosion is found to be due to adsorption of the extract of pomelo peels on the metal surface which is in conformity with Langmuir's adsorption isotherm.

1. Introduction

The corrosion protection of metals has received much attention globally due to massive losses of natural resources and finances due to corrosion. Mild steel is the most common form of steel because of its relatively low cost and material properties that are acceptable for many applications particularly in food, petroleum, chemical and electrochemical industries, and power production[1, 2].

The major problem of mild steel in many industries is its dissolution in the acidic medium where acids are broadly used for applications such as acid pickling, acid cleaning, acid descaling, and oil well acidizing [3, 4].

Corrosion inhibitors are commonly used in industry to control metal dissolution and reduce the corrosion rate in contact with the aggressive acid solution. Most acid inhibitors are organic compounds containing nitrogen, sulfur, and oxygen in their molecule [5-8]. The inhibition action is due to the formation of protection film on to the metal surface blocking the metal from the corrosive agents present in solution. A large number of scientific studies have been dedicated to the corrosion of mild steel and the use of organic compounds as corrosion inhibitors in acidic media [9-12]. Because most of these synthetic organic inhibitors are expensive and toxic to the environment, investigation and evaluation of naturally occurring substances (organic inhibitors) have continued to receive attention due to the presence of hetero atoms like nitrogen, sulfur, and oxygen in their structure.

The study of plant extracts as low-cost and ecofriendly corrosion inhibitors have been interested most researchers due to an environmental perspective. Green corrosion inhibitors have a promising future for the quality of the environment because they do not contain heavy metals or other toxic compounds. Also, they are a biodegradable and renewable source of materials.

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Numerous reports have been highlighted in the successful application of plant extracts as corrosion inhibitors for mild steel in different media [13-17]. Naturally occurring molecules exhibiting a strong affinity for metal surfaces are the focus of research oriented toward the development of environmentally friendly corrosion inhibitors; compounds showing good inhibition efficiency and low environmental risk. The efficiency of these organic corrosion inhibitors is related to the presence of polar functional groups with S, O or N atoms in the molecule, heterocyclic compounds, and pi electrons.

One of these natural compounds is fruits. Fruit is a rich source of chemicals such as vitamins, minerals, and phenolic compounds. Pomelo fruits are one of the traditional fruit of Asian region, particularly in South East Asia. Pomelo fruits growth and eats in almost all of the province in Indonesia. However, their peels have not been yet utilized. Since pomelo peels have high enough tannin, which is one of good inhibitor compound. Hence, the investigation of pomelo peels extracts as corrosion inhibitor would be giving alternative utilization of pomelo fruits.

The aim of this study is to investigate the efficiency of extract pomelo peels in inhibiting corrosion of mild steel in hydrochloric acid solution. Various concentration of pomelo peels extract and immersion time will be examined.

2. Methodology

The corrosion behavior of mild steel in hydrochloric acid was investigated by gravimetric method. The mild steel was purchased from the local supplier, while hydrochloric acid was purchased from Merck Chemical, and pomelo fruit was obtained from the local market in Lhokseumawe.

2.1. Specimen Preparation

Rectangular mild steel specimens with dimensions of 5x3x0.2 cm were used for corrosion investigation. The specimen's surfaces were abraded with silicon carbide abrasive papers ranging from 400 to 1200 grits. The sample was then degreased with acetone, washed in a stream of water and dried in the air and then immersed in the hydrochloride acid 1 M with the absence and the presence of inhibitor.

2.2. Inhibitor Preparation

Pomelo peels were collected from pomelo fruit. They were cut in a small piece and dried naturally in the atmospheric environment and then continue dried at 40^{o}C in the oven. Dried pomelo peels ground to powdered form and weighed 500 grams. The powders were immersed in 1000 ml ethanol 96% and maceration for 48 hours. The extract was filtered through Whatman filter paper. The filtrate was evaporated using rotary evaporator. The solutions were cooled and then stored. From the respective stock solutions, inhibitor solutions were prepared at the concentration ranging from 0.4 to 1.6 v%.

2.3. Measurement rate of corrosion

The gravimetric experiments were carried out according to the ASTM practice standard G-31 [18]. Before conducting the experiments, the pre-cleaned specimens were weighed on an analytical balance using 0.1 mg precision. The considered samples were immersed in the corrosive medium with and without inhibitors at various immersion time. At the end of the experiment, the specimens were removed from the corrosive medium and rinsed with water, cleaned with acetone, dried in hot air and finally weighed. The mean of weight loss values of three identical specimens was used to calculate the corrosion rate and inhibition efficiency of the inhibitor. Corrosion rate was calculated using the formula given in Eq. 1.

$$CR = \frac{K \, x \, W}{A \, x \, T \, x \, D} \tag{1}$$

Where CR is corrosion rate in mm/y, K is a constant, 87600, W is mass loss in g, A is the area of immersed samples in cm^2, T is time of exposure in hour, D is density of mild steel specimen in g/cm^3.

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Inhibition efficiency and surface coverage (θ) were also determined using Eqs. 2 and 3.

$$\mathrm{IE} = \frac{\text{CR uninhibited} - \text{CR inhibited}}{\text{CR uninhibited}} \text{ x } 100\% \qquad (2)$$

Where IE is inhibition efficiency (%), $CR_{uninhibited}$ is corrosion rate without using inhibitor and $CR_{inhibited}$ is corrosion rate with using inhibitor.

$$\theta = \frac{\text{CR uninhibited} - \text{CR inhibited}}{\text{CR uninhibited}} \qquad (3)$$

Where θ is surface coverage, $CR_{uninhibited}$ is corrosion rate with the absence of inhibitor and $CR_{inhibited}$ is corrosion rate with the presence inhibitor.

2.4 SEM Analysis

The surface morphology of the mild steel before and after immersion in the acid solutions (with and without the extracts) was examined using a JSM-6510 LA, a JEOL analytical low vacuum scanning electron microscope.

3. Result and Discussion

The measurement of corrosion rate is conducted by weight loss method which has broad practical applications [19-21]. The rate of corrosion can be defined as the ratio of the weight loss of the samples to its area and the immersion time as given in Eq. 1. The advantage of this method is its relative simplicity and availability. Furthermore, the method uses a direct parameter for quantitative evaluation of corrosion i.e. mass loss of metal. The effect of the inhibitor on the corrosion rate of mild steel in HCl 1M without and with different concentration of pomelo peels extract is shown in Fig. 1. It can be seen that the corrosion rate decreases significantly with the increasing of inhibitor concentration. The rate of corrosion in the absence of pomelo peels extract is 8.87 mm/y at five days immersion time. While in the presence of 1.6% pomelo peels extract, the corrosion rate reduces to 0.69 mm/y. Decreasing of corrosion rate is due to the formation of the layer on the metal surface which covering the surface metal contact the metal with the corrosive environment [22, 23].

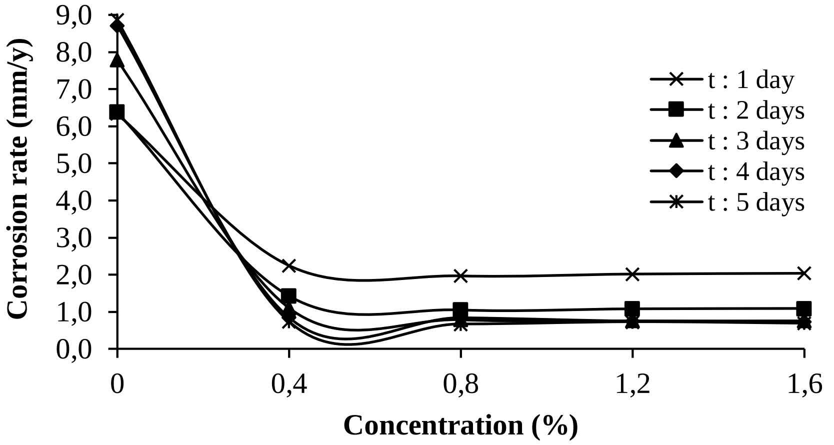

Figure 1. Effect of inhibitor concentration on corrosion rate of mild steel in HCl 1 M

The effect of immersion time on the corrosion rate of mild steel in HCl 1M at various concentration of pomelo peels extracts is presented in Fig. 2. It can be seen that in the absence of pomelo peels extract, the rate of corrosion increase with the increasing of immersion time. In the first day, the corrosion rate is 6.34 mm/y and then rise to 8.87 mm/y in the fifth day. This phenomenon occurred due to the intensive

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dissolution of metal in the corrosive media in the lapse time. On the other hand, with the presence of pomelo peels extracts, the corrosion rate decrease with increasing immersion time. The corrosion rate using pomelo extracts 1.6% are 2.04 mm/y and 0.69 mm/y at the first day and the fifth day, respectively.

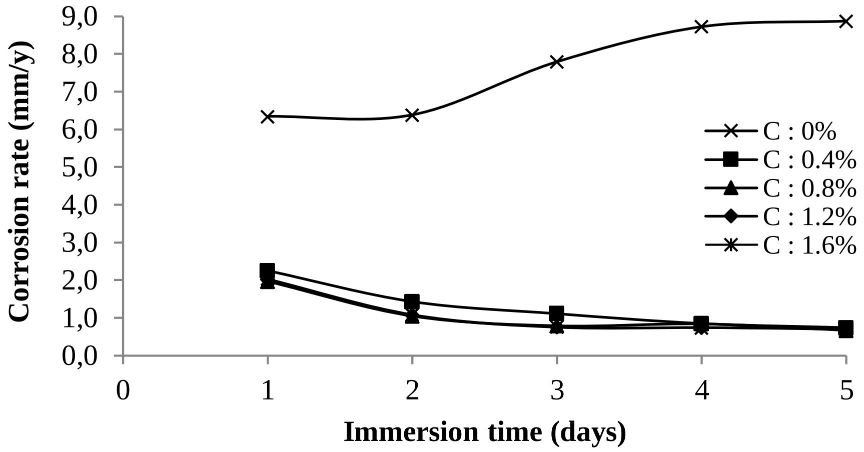

Figure 2. Effect of immersion time on corrosion rate of mild steel in HCl 1 M

The inhibition efficiency of pomelo peels extracts for mild steel in HCl 1M acid solution is presented in Fig. 3. The graph reveals that the inhibition efficiency of pomelo peels extract increase with the increase of concentration and immersion time. The highest value of inhibition efficiency is reaching of 92.22% at the concentration of 1.6% and immersion time five days. This phenomenon can be attributed to the increase of the surface covered, and that due to the adsorption of natural compounds on the surface of the metal, as the inhibitor concentration increases. The result is in good agreement with other's [14, 24].

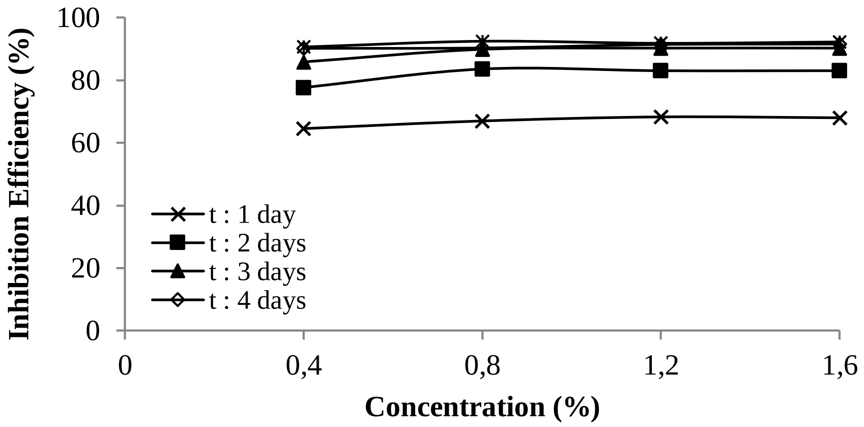

Figure 3. Inhibition efficiency of Pomelo peels extract on mild steel in HCl 1M

Adsorption isotherms are very important to understand the mechanism of inhibition corrosion reactions. The most frequently used isotherms are Langmuir [25, 26], Frumkin [27, 28], and Temkin [29, 30]. The Langmuir isotherm assumes that there is no interaction between adsorbed molecules on the surface. The Frumkin adsorption isotherm assumes that there is some interaction between the adsorbates, and the Temkin adsorption isotherm represents the effect of multiple layer coverage. Fig. 4 shows adsorption isotherm of pomelo peels extracts concentration. It can be seen from the graph that the curve obtained shows fit well with Langmuir adsorption isotherm. Hence, the adsorption of pomelo peels extracts on the surface of metal occurs in a single layer.

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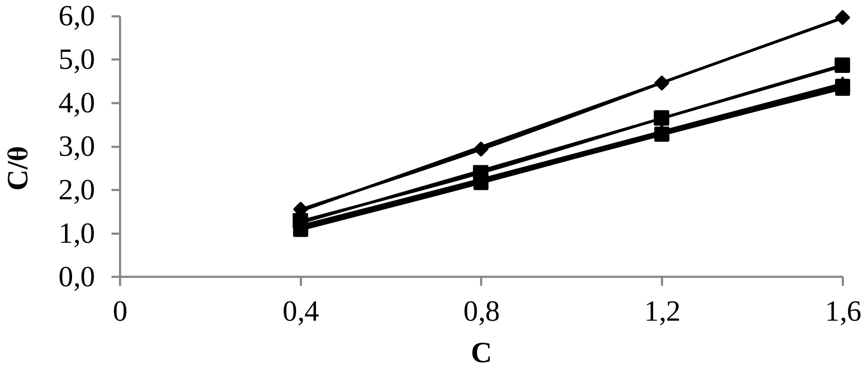

Figure 4. Mechanism of corrosion inhibition

Scanning electron microscopy (SEM) of the samples in the absence and presence of pomelo peels extract were shown in Fig. 5. Fig. 5(a) shows the cleaned sample of mild steel before immersion in HCl 1 M solution. It can be seen that the surface of metal has the smooth surface with some scratch due to polishing work. While in Fig. 5 (b) represent the corrosion of mild steel due to the interaction with HCl 1 M solution in the absence of inhibitor for one day. It shows that the rough surface on the surface of mild steel which means the metal is corroded. Furthermore, Fig. 5 (c) reveals the morphology of the mild steel surface which is immersed in HCl 1 M solution and inhibitor 1.6% for one day. It shows that there is a smooth surface on mild steel surface compare to with the absence of inhibitor. This result confirms that the extract prevents the corrosion of mild steel through adsorption of the inhibitors on the metal surface.

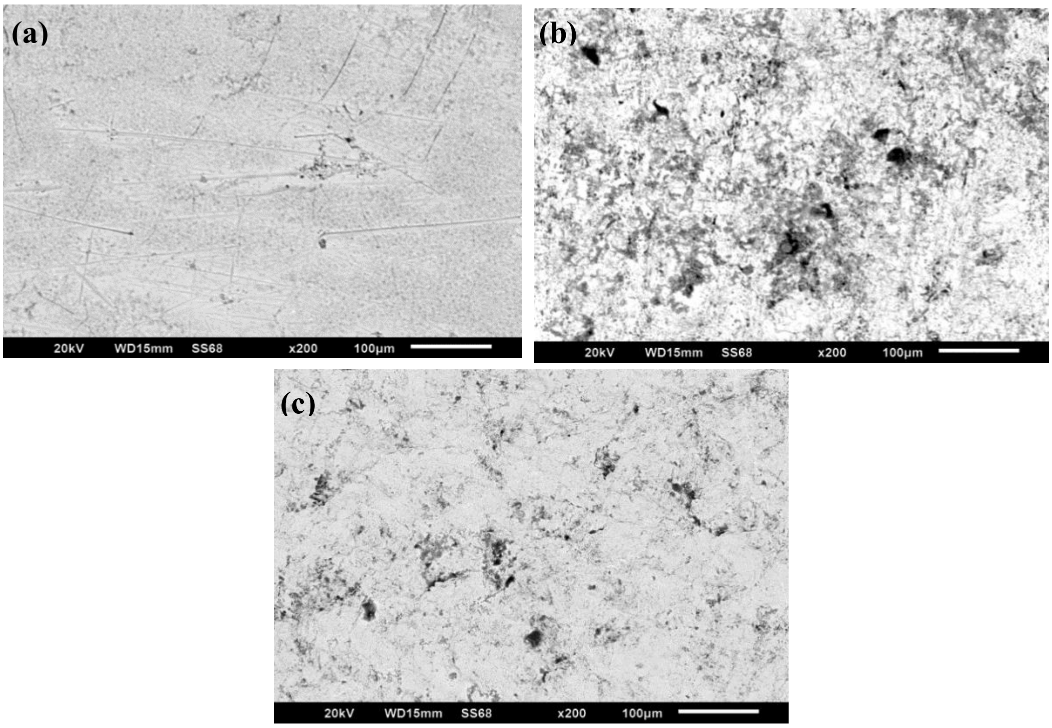

Figure 5. SEM image of samples

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4. Conclusion

The corrosion rate decrease with the increasing of pomelo peels extracts concentration. The inhibition efficiency of the pomelo peels extracts on corrosion inhibition increases with increase in the concentration of extract. The highest efficiency obtained at 1.6% extract concentration which is 92.22%. The mechanisms of inhibition follow Langmuir's adsorption isotherm. SEM study shows that the inhibitor covers the surface of the metal. The results of the studies confirmed that the pomelo peels extract have potential to prevent the corrosion of mild steel in the acidic environment.

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