The potential of Petai peel as a zinc corrosion inhibitor in sodium chloride solution

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Abstract

The use of corrosion inhibitors is one of the methods for metal protection in acidic media and salt media. At present, the organic corrosion inhibitor is widely used in industry, because organic inhibitors are more environmentally friendly than inorganic inhibitors. One of the organic corrosion inhibitors is the Petai peel (*Parkia speciosa*). This study aims to apply the Petai peel as a zinc corrosion inhibitor in sodium chloride (NaCl) solution. This research applies Petai peel as an inhibitor in 3 forms, namely in the form of powder, extract, and tannin. Petai peel is used as a corrosion inhibitor because it contains tannins. The influential variables in this study include the inhibitors form, inhibitors concentration, and duration of immersion. The concentrations of inhibitors used are 2%, 4%, and 6% (w/v), respectively, and the immersion time in 3% NaCl solution varied up to 12 days. The measured parameters are corrosion rate and inhibition efficiency. The results showed that the three forms of inhibitors with a concentration of 2% are able to reduce the rate of corrosion of zinc in the NaCl solution, but the corrosion rate would decrease with increasing concentration of the inhibitor. During 12 days immersion, the lowest corrosion rate of zinc is 1.46 mpy, and the best inhibition efficiency is achieved at 90% on the third day.

Keywords: tannin, corrosion rate, inhibition efficiency, Petai peel, zinc, *Parkia speciose*.

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Introduction

Corrosion is a complex phenomenon that occurs as a result of interactions between water and metal surfaces, and to overcome this can be done using inhibitors. At present, corrosion inhibition by organic inhibitors is widely used in industry, because organic inhibitors are more environmentally friendly than inorganic inhibitors [1, 2]. Most organic inhibitors control corrosion by adsorbing inhibitor molecules on the metal surface that form a thin layer. The use of inhibitors is one of the most practical methods for metal protection in acidic media and salt media. Corrosion inhibitors are typically used to increase the duration of use of materials [3, 4]. Some researchers have reported the use of natural inhibitors which is extracted from the leaves or seeds of a plant [5–9].

This encourages the need to develop the use of natural organic inhibitors. Basically, plants that can be used as organic inhibitors are plants that have antioxidant properties, such

as containing flavonoid compounds, tannins, ascorbic acid, phenolic, and others. In this study, Petai peel (*Parkia speciosa*) is used as the main component of zinc corrosion inhibitors. Petai plant is a plant that is widely available in Indonesia, where the Petai fruit peel is still a waste that has never been utilized. This Petai peel is antioxidant and has polyphenol compounds. The polyphenol compound contained in the Petai peel that can be used as an inhibitor is tannin [10]. The tannin as a corrosion inhibitor plays a role by covering the surface of zinc to form a passive layer on the cathodic side so that it affects the cathode reduction reaction. Zinc oxidation reaction at the anode will be inhibited if the reaction at the cathode is inhibited. The passive layer formed will prevent the entry of corrosion ions to the zinc surface, so that the corrosion rate of zinc will decrease.

Studies on the application of tannins as inhibitors of zinc metal have been carried out by previous researchers. El-Etre *et al.* (2005) reported that the extract of *Lawsonia* leaves containing tannin can act as a good inhibitor for the corrosion of zinc in NaCl and NaOH solutions [11]. Ugi *et al.* (2015) also have reported the results of their study of tannin application from *Mangifera indica* leaves on zinc sheet in H₂SO₄ solution. They report that tannin as a corrosion inhibitor can achieve zinc corrosion inhibition efficiency of 70.6% [12].

The use of Petai peel as a corrosion inhibitor is divided into 3 forms, namely in the form of Petai peel powder, Petai peel extract form, and the form of tannin from Petai peel. This treatment is carried out to determine the ability of Petai peel as a zinc corrosion inhibitor, whether the Petai peel must be extracted into tannins, or it can be used directly in the form of Petai peel powder or in the form of Petai peel extract.

Experimental

Making of tannins, concentrated extracts, and Petai peel powder

Firstly, the Petai peel is cleaned of impurities, then cut into small pieces and dried in the open air. Peel that has been dried is blended to become powder. This Petai peel powder is put into the maserator, then 1:9 (w/v) methanol is mixed, then left in the maserator for 24 hours. After that filtered with filter paper. The obtained filtrate is put into a rotary vacuum evaporator at a temperature of 64°C–66°C for 2 hours. Then the concentrated extract is put into a glass bottle, then tested qualitatively. Qualitative analysis is done by putting the 10 g extract into the beaker glass, then adding 10 mL of water. Ten drops of FeCl₃ 1% solution is added to the filtrate to test for the presence of tannin. If there is a change in color to blackish green, then this indicates the presence of tannins.

Concentrated extract is put into the beaker glass then added 95% ethyl acetate, stirred until mixed, allowed to stand to form a precipitate, and then filtered. The precipitate obtained is washed again with 95% ethyl acetate until the filtrate is clear, then filtered to obtain the residue. The residue obtained is tannin which is ready to be used as an inhibitor in extract form.

In preparation of the zinc plate which will be tested, zinc plates as samples with a size of 1×2×0.06 cm smoothed the surface with sandpaper, then washed with detergent and

distilled water, and dried in an oven at 110°C for 2 hours. The zinc plate used as a sample in this study is a zinc alloy, and the composition of the zinc plate can be seen in Table 1. Immersion of zinc plate is carried out on sodium chloride (NaCl) without inhibitors and on NaCl solution with inhibitors. The concentration of NaCl used in this study is 3%. At immersion zinc plate without inhibitor, the zinc plate is immersed in NaCl solution with a volume of 50 mL for 3 days, 6 days, 9 days and 12 days, then the rate of corrosion reaction is determined.

The immersion the zinc plate with an inhibitor is also carried out on the NaCl solution with a volume of 50 mL. Inhibitors used are tannins from Petai peels, Petai peel extracts, and Petai peel powders. The inhibitor concentrations added are 2%, 4%, and 6% (w/v), respectively, and immersed for 3 days, 6 days, 9 days, and 12 days, then the corrosion reaction rate and the inhibition efficiency of each variation were determined.

The calculation of the corrosion rate

After the corrosion process has been running for a certain time, the corrosion product is removed from the corrosion media, then washed and dried in an oven at 110°C, then weighed as the final weight. The initial weight of zinc is the weight of zinc before being immersed in solution. Corrosion reaction rate and corrosion inhibition efficiency are calculated by equation 1 and equation 2 [13].

$$CR = \frac{KW}{DA t} \quad (1)$$

where K is a constant ($3.45 \cdot 10^6$); CR is corrosion rate (mils/year, mpy); W is lost mass (g); D is density (g/cm^3); A is surface area (cm^2), and t is time (hour).

$$\text{Inhibition Efficiency} = \frac{CR_0 - CR_i}{CR_0} \cdot 100\% \quad (2)$$

where CR_0 is corrosion rate without inhibitors, and CR_i is corrosion rate with inhibitors.

The procedure of SEM-EDX (JEOL JSM-6510LA) analysis

Carbon tape is attached to the specimen mount to place the sample, then setting the surface height of the sample is the same as the surface height of the specimen holder. The specimen holder is selected and the height of the sample is filled in the standard setup menu, and the working distance is adjusted. Observation is done by adjusting the sample magnification, resolution, focus, stigmator, object position, and size. After the SEM observation is carried out, then an EDX analysis is performed.

Results and Discussion

The result of Fourier Transform Infrared analysis on Petai peel

Based on the results of analysis with Fourier Transform Infrared (FTIR) (Figure 1), Petai peel powder showed the presence of tannin as indicated by the presence of hydroxyl (OH) groups at the absorption peak with wave numbers 3421.72 cm^{-1} [14] and aromatic carbonyl groups (C=C) with the absorption wave number 1620.21 cm^{-1} [15]. The results of the FTIR analysis in this study are similar to the results of the analysis conducted by Zhao, *et al.* [14], while the determination of tannin quality is identified by qualitative analysis using FeCl_3 solution. The results of the analysis of the Petai peel extract gave a greenish-black precipitate on hydrolyzed tannins [8]. Based on the extraction results, it is found that the Petai peel contained 9.74% tannin.

Figure 1. Petai peel analysis by using FTIR.

Effect of Petai peel powder as inhibitor of zinc plate

Figure 2 shows that the Petai peel powder can reduce the corrosion rate of zinc in NaCl solution. From the results of the study it is found that the higher the concentration of Petai peel powder, the rate of corrosion of the zinc plate in the NaCl solution would be lower. This means that the Petai peel contains an inhibitor that can reduce the corrosion rate. The results obtained showed that the addition of 4% and 6% of Petai peel powder give a comparable corrosion rate. Hence, Petai peel powder can be used as a zinc inhibitor in NaCl solution.

Figure 2. Effect of immersion time using Petai peel powder as an inhibitor of zinc plate corrosion rate.

In Figure 3 can be seen the efficiency of zinc corrosion inhibition by the addition of Petai peel powder as an inhibitor. The results obtained indicate that the efficiency of inhibition is influenced by the concentration of the inhibitor and the length of immersion time [16]. In the use of Petai peel powder as an inhibitor, the highest inhibition efficiency obtained is 51.96%.

Figure 3. Effect of Petai peel powder as inhibitor on the efficiency of zinc corrosion inhibitors.

Effect of Petai peel extract as inhibitor of zinc plate

In Figure 4 and Figure 5 can be seen the corrosion rate and the efficiency of zinc inhibition in the use of Petai peel extract as an inhibitor. Same as in Figure 2 and Figure 3, the corrosion rate decreases and efficiency increases with increasing levels of inhibitors and the duration

of immersion. This is because the more hydroxyl groups that interact with zinc to form a layer will cause the rate of corrosion to decrease [16, 17]. The results show that the highest inhibition efficiency of 79.41% is obtained with the addition of 6% Petai peel extract.

Figure 4. Effect of immersion time using Petai peel extract as an inhibitor of zinc plate corrosion rate.

Figure 5. Effect of peel Petai extract as inhibitor on the efficiency of zinc corrosion inhibitors.

Effect of Petai peel tannin as inhibitor of zinc plate

Figure 6 and Figure 7 are the corrosion rate and zinc inhibition efficiency by using tannins from Petai peels as inhibitors. In Figure 6 can be seen that the addition of 2% tannin is good enough to inhibit the rate of corrosion, but the lowest corrosion rate is achieved by adding 6% of tannin. The highest efficiency of 90.19% is achieved when adding 6% of tannin with a soaking time of 3 days.

Figure 6. Effect of immersion time using Petai peel tannin as an inhibitor of zinc plate corrosion rate.

Figure 7. Effect of peel Petai tannin as inhibitor on the efficiency of zinc corrosion inhibitors.

Results of surface analysis and composition of zinc plates by using scanning electron microscope–energy dispersive X-ray (SEM-EDX)

In this study, the surface structure and surface element composition of the zinc plate is tested by using SEM-EDX. Figure 8 is a photograph of SEM results with 1000 times magnification of the zinc surface before immersion (a), after immersion with tannin inhibitors of 6% for 12 days (b), and after immersion without inhibitors for 12 days (c). In Figure 8a, the surface of the zinc plate is still smooth because the plate has not been influenced by the environment. In Figure 8b, the surface of the zinc plate is still smooth, but there are small cracks and tannin compounds attached to the surface of the plate. This is due to tannin compounds inhibiting corrosion, while in Figure 8c, the surface of the zinc plate is seen to be uneven and rough

because corrosion that occurs on the surface of the plate occurs without obstacles so that the entire surface forms corrosion.

Figure 8. Zinc surface before immersion (a), after immersion with tannin inhibitors (b), after immersion without inhibitor (c).

EDX analysis results on the zinc plate

Figure 9 is the result of testing by using EDX for zinc plates before immersion (a), after immersion for 12 days with the addition of tannin inhibitors of 6% (b), and after immersion for 12 days without the addition of inhibitors (c). The composition of the chemical elements on this zinc plate is summarized in Table 1, Table 2, and Table 3.

Table 1. Composition of chemical elements on zinc plates before immersion.

Element	keV	Mass (%)
C	0.277	14.15
O	0.525	9.57
Al	1.486	0.79
Zn	8.630	75.49
Total		100

Table 1 shows the element Zn as a chemical element making up the zinc plate has a content of 75.49%. But in Table 2 and Table 3 it can be seen that the percentage of Zn elements tends to decrease because Zn elements and their solutions form corrosion such as ZnO , Zn(OH)_2 and $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ [18].

The existence of other elements such as P, S, Al, Fe, Ca, K, and O in the analysis results can be caused by these elements attached to the plate when the analysis process is done by using SEM-EDX. The elements carbon (C) and oxygen (O) in Table 3 increase compared to Table 1 because the corrosion formed removes the element Zn, making elements C and O become more dominant.

Figure 9. EDX spectra of zinc surface plate before immersion (a) after immersion with tannin inhibitor (b), after immersion without inhibitor (c).

Table 2. Composition of chemical elements on zinc plate after soaking for 12 days with the addition of tannin inhibitors of 6%.

Element	keV	Mass (%)
C	0.277	23.21
O	0.525	9.57
Cl	2.621	0.56
Ca	3.690	0.63
Fe	6.398	0.48
Zn	8.630	65.55
Total		100

Table 3. Composition of chemical elements on zinc plates after immersion for 12 days without the addition of inhibitors.

Element	keV	Mass (%)
C	0.277	35.80
O	0.525	21.73
K	3.312	0.23
Ca	3.690	0.63
Fe	6.398	3.90
Zn	8.630	35.49
Al	1.486	0.78
P	2.013	0.73
S	2.307	0.19
Total		100

Conclusion

Based on the research results, it can be concluded that Petai peel contains tannin which can be used to inhibit zinc corrosion in NaCl solution. Petai peel application in the form of powder, extract and tannin can inhibit zinc corrosion. The higher the concentration of inhibitors used, the corrosion rate decreases, and corrosion inhibition efficiency increases. The corrosion rate of zinc also decreases with increasing immersion time. Corrosion inhibition efficiency in this study can reach up to 90%, therefore, Petai peel has great potential to be used as corrosion protection in the coating industries.

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