The inhibitive effect of tannin in *Psidium guajava* leaves towards 304SS corrosion in concentrated HCl

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Abstract. Tannin isolated from *Psidiumguajava* leaves are developed to enhance the corrosion protection of austenitic stainless steel. It is used as a green inhibitor, extracted from *Psidium guajava* which grow in East java, Indonesia. In the present work, the corrosion inhibition properties of the tannin inhibitors were investigated in 3M HCl by polarization potentiodynamic measurements. The result reveals that tannin 1g/L could enhance the inhibition efficiency up to 91.81%.

1 Introduction

Acid solutions are often used for cleaning the surface of any part of machines from scales in industry. Austenitic steel is widely used in the chemical, petrochemical and petroleum industry, due to their good resistance to corrosion[1, 2]. However, the aggressiveness molecules in acid solutions can cause the retardation attack of austenitic steel [2]. Recently, corrosion inhibitor from plant extracts have magnetized attention of researcher due to their eco-friendly properties, economical and simple production. The green corrosion inhibitor from plant extracts is found to be highly efficient in acidic medium [3 – 10]. The inhibitor forms protective layer on the metal surfaces with an adsorption mechanism on the oxide films [11, 12]. In this present work, we use *Psidium guajava* leaves as a green inhibitor, as we know that this plant is richly growth in Indonesia. Several studies on the use of psidiumguajava leaf extract have been various corrosive environments such as NaCl [13], HCl [14], HNO₃[5]. In the previous study, many of the solutions used were dilute. Therefore, in this study conducted a thick corrosive solution, to know the ability of psidiumguajava inhibitors in a concentrated acid solution. There is still lack report using it as corrosion inhibitor for austenitic steel in concentrated HCl. In addition, in this work we will study the inhibition effect of *Psidisium guajava* leaves extract on the metal surface of 304SS in 3M HCl.

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2 Experimental

2.1 Materials

The austenitic steel used in the present work (composition (wt%) = C, 0.08%; Mn, 2.00; P, 0.045; Si, 1.00; Cr, 18.00; Ni, 8.00; Fe, balance) was 304 SS type with the dimension of 25 mm × 20 mm × 5 mm. The surface of the steel specimens was smoothed with 600-, 800-, 1500-grit sand papers to make the surface smooth.

2.2 Synthesis of inhibitor and corrosive Environment

The inhibitor was extracted from dried *Psidium guajava* leaves which were collected from Kemantren village, Sidoarjo, Indonesia. The dried leaves then were cleaned and grounded into powder. The 10 g of leaves powder was dissolved in 96% ethanol (250 mL). The aqueous extract was stirred at 50°C for 150 minutes. The filtrate obtained then dried to get the powder form. The corrosive media of 3M HCl was prepared by dilution of AR grade 37% HCl (Merck) using distilled water.

2.3 Characterization of inhibitor

The *Psidium guajava* extract was characterized by FTIR characterization. The FTIR test uses the Shimadzu IR Prestige -21 brand. Pellet PG extract test sample was mixed with KBr with a ratio of 1: 100.

2.4 Weight loss testing

Dimension specimen size 25x20x5 mm. The specimens were immersed in 3M HCl solution for 10, 15 and 20 days. The specimen is smoothed on the surface with a sand paper grade of 600-1500. The specimens were weighed using digital scales type DS-671 Kenko. The amount of inhibitor used was 0.2; 0.4; 0.6; 0.8; 1 g / L. The corrosion rate is calculated using the equation 1[16]

$$Cr_{(mm/yr)} = \frac{87.6 \times w}{D \times A \times t} \quad (1)$$

Where D is the steel density in gcm^{-3} , w is calculated based on the difference between initial and final weight (mg), t is the time of immersion (hour), and A is the area of the specimen (cm^2).

After obtaining optimum inhibitor concentration from weight loss test, then electrochemical measurement. The electrochemical measurement of 304SS with and without inhibitor in 3M HCl. solutions were studied using three electrode cell with an Ag/AgCl (3M KCl) reference electrode and a platinum as the counter electrode, performed using Autolab PGSTAT302N. Potentiodynamic polarization tests were performed a scanning rate of 0.001 V/s from -1V to +1V with respect open circuit potential (OCP). The corrosion rate was calculated according to ASTM G 102-89.

Tafel polarization parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic Tafel slope (b_a), cathodic Tafel slope (b_c), and inhibition efficiency (IE) are listed in Table 1. The inhibition efficiency was calculated using the following equation [12,17-19]:

$$IE\ (\%) = \frac{I_{corr}^o - I_{corr}}{I_{corr}^o} \times 100 \tag{2}$$

where I_{corr}^o and I_{corr} are the corrosion current densities in the absence and presence of inhibitor.

3 Result and Discussion

3.1 FTIR characterization

FTIR spectroscopy is used to understand the bonding interaction of the inhibitor is represented in Figure 1. The spectra indicate the presence of characteristic band at 3270.41cm⁻¹(O-H group), 2911.81, 2879.40, 1414.13, and 1322.30 (C-H group), 1544.18 and 1510.92 (C = C group), 1328.63, 1255.34, 1288.22, 1201.4, 1105.28, and 1046.30 (C – O group). These characteristic band show the similarity with functional group which are contained in tannin of *Psidium guajava* leaves. It is kind of flavan-3,4-diol molecule.

3.2 Weightloss Method

Fig. 1. The relationship of immersion time to inhibition efficiency in various concentrations of psidium guajava by weight loss method

The weight loss results show that the greatest inhibition efficiency is in the addition of 1g / L psidium guajava. Based on Figure 1 it is known that the efficiency of inhibition increases with the addition of inhibitor concentration. At various immersion times it was seen that the greatest inhibition efficiency was in addition of 1 g / L inhibitor. The efficiency of inhibition increases with the addition of inhibitor concentration. At various times of SS304 steel immersion, the same pattern of inhibition efficiency increases. Inhibition efficiency increases with increasing concentration of inhibitor. At the highest concentration of 1 g / L, guava psidium inhibitor corrosion rate has the greatest inhibitory

efficiency ie 72.01%. Therefore, it is necessary to continue electrochemical testing on the addition of 1g / L inhibitor concentration. Maximum inhibition efficiency was obtained at 15 days immersion time of 72.01%. Increased inhibition efficiency decreases with increasing inhibitor concentration, as well as with time. The efficiency of inhibition on the immersion of 20 days has the smallest inhibitory efficiency. This is due to the presence of desorption by the inhibitor molecule of the metal surface [15]. This shows that the adsorption is physisorption. While chemisorption shows the amount of energy and immersion time [20]. Figure 1 shows the inhibition efficiency is increasing with increasing inhibitor concentration. This is caused by the interaction of the inhibitor molecule is greater than the interaction inhibitors on metal surfaces [21].

3.3 Potentiodynamic polarization

Figure 2 shows the Tafel curves of the 304SS in 3M HCl with or without *Psidium guajava*inhibitor. The addition of inhibitor changes the shapes of the anodic and cathodic Tafel curves significantly. Optimum inhibition efficiency data was obtained with addition of 1g /L Psidium guajava extract. Thus, electrochemical testing is represented by specimen testing on the addition of 1g / L inhibitor.

Table 1. Electrochemical parameters for 304SS in the absence and presence of inhibitor

Concentration (g/L)	b_a (mV/dec)	b_c (mV/dec)	Ecorr (mV)	Icorr ($\mu A/cm^2$)	C_R (mmpy)	EI (%)
Blank	438.71	246.9	-297.32	132.52	153.96	0
1	266.74	70.19	-283.52	10.85	12.61	91.81

Fig. 2.Tafel curve of SS 304 in 3M HCl

Measurement of inhibitory efficiency at the addition of 1 g / L inhibitoe concentration has an efficiency of 91.81 %. The E_{corr} shifted 14 mV to the right, indicates that inhibitor act as mixed typed inhibitor. Because the E_{corr} values just displaced less than ± 85 mV [22]. The corrosion density also decreases with the presence of the inhibitor from 132.52 $\mu A/cm^2$

to $10.85 \mu\text{A}/\text{cm}^2$. The current density of is proportional to the corrosion rate. Furthermore, the value of the corrosion current density is used to calculate the efficiency of inhibition. The efficiency of the inhibition obtained increases as the inhibitor concentration increases. The results of the weight loss and potentiodynamic polarization methods show an increase in inhibitory efficiency with the addition of psidium guajava extract inhibitors.

Fig. 3. The schematic illustration of tannin inhibitor on the 304SS interface

Figure 3 shows the mechanism of 304SS surface inhibition. From FTIR results reveal that the functional groups contained in *Psidiumguajava* extract have the similarity with tannin. Tannins have a lot of polyphenol compounds that can inhibit the oxidation process and decrease the corrosion rate. Tannin probably protect the 304SS surface by forming layer at the metal acid interface as shown in Figure 3[12].

4 Conclusion

The results of the present study revealed that tannin in *Psidiumguajava* leaves functioned as a good corrosion inhibitor for 304SS in 3M HCl. The best inhibition efficiency which were got from weight loss method, reached with the addition of 1 g/L of *Psidium guajava* leave extracts. The inhibition efficiency reaches up to 91.81% by the addition of g/L *Psidiumguajava* leaves extract .

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