WCEJ

WORLD CHEMICAL ENGINEERING JOURNAL

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The Effect of Immersion Time on The Ability of Tannins to Inhibit The Corrosion Rate of Mild Steel in 1M H_2SO_4 Solution

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ARTICLE HISTORY

Received May 2, 2020
Received in revised form May 24, 2020
Accepted June 19, 2020
Available online June 20, 2020

ABSTRACT

Tannin is a polyphenol compound that is widely found in various types of plants. Polyphenol compounds can inhibit the corrosion rate of mild steel. This study aims to determine the effect of immersion time on tannins' ability to inhibit the corrosion rate of mild steel in 1M sulfuric acid. The method used is weight loss with immersion time variations of 2,4 and 6 hours, temperature variations of 313K, 333K, and 353K. The concentration variation used was 0; 250; 500; 750; 1000; 1250 ppm. The research results found that the immersion time affected tannins' ability to inhibit corrosion in mild steel. The highest efficiency was 71.07% at a concentration of 1250 ppm and 313K. The longer the immersion time, the lower the tannin ability to inhibit corrosion in mild steel.

Keywords: *Tannin, inhibitor, mild steel, sulfuric acid, corrosion*

1. INTRODUCTION

Corrosion is a natural process that cannot be avoided, but the rate of corrosion can be minimized. In industry, metal use cannot be avoided, so it is necessary to protect against metal from corrosion. One of the efforts that can be made to minimize corrosion is the use of corrosion inhibitors. An inhibitor is the addition of several chemicals into the fluid to reduce the rate of corrosion. Inhibitors work by making blocks between metal materials and the environment. The current Inhibitors widely used are phosphate or sulfite, which cause a rise in pH. The use of environmentally friendly, highly protective, and non-toxic inhibitors continues to grow. Tannin is a material that continues to be developed because of its renewable, non-toxic properties and its ability to work in a conductive/corrosive environment that is much higher (8,000 µS / cm to 10,000 µS / cm) than ASME guidelines (<3,000 µS / cm)(Dargahi, Olsson, Tufenkji, & Gaudreault, 2015).

Structurally, tannins are phenolic compounds with a large molecular weight consisting of a hydroxyl group and several related groups such as carboxyls to form strong significant complexes with proteins and some macromolecules. Tannins are found in almost every part of the plant, namely bark, leaves, fruit, and roots.

Tannin is widely found in plants, both in the leaves, stems, and fruit. Based on research, the tannins contained in plant extracts can inhibit the rate of corrosion. Tannins are polyphenolic macromolecular compounds that come from various types of plants. Inhibition of tannins in metals is to form complex groups with metal ions. The complex groups are chemical bonds that then prevent corrosion events on the metal surface.

Previous studies using plant extracts as bio inhibitors of corrosion include *mimosa tannins* on carbon steel in sulfuric acid solution(Martinez & Štern, 2001), *mangrove tannins* in mild steel in acid solution(Adam, Rahim, & Shah, 2014), *Mahaleeb seed* extract on carbon steel in acid solution(Ganash, 2019), *Ircinia strobila crude* extract in mild steel in acid solution(Fernandes et al., 2019), *Tagetes erecta* extract on mild steel in acid solution(Mourya, Banerjee, & Singh, 2014), *Citrus aurantium* extract on mild steel in sulfuric acid(Hassan, Khadom, & Kurshed, 2016), *Sunflower seed hull* extract in mild steel in chloride acid(Hassannejad & Nouri, 2018), *Cuscuta reflexa* extract on mild steel in sulfuric acid(Saxena, Prasad, & Haldhar, 2018), *Litchi peel* extract on mild steel(Ramananda Singh, Gupta, & Gupta, 2015). The results showed that the plant extracts could reduce each material's corrosion rate in its corrosive media. Research on the ability of plant extracts as a corrosion inhibitor material continues to be developed.

In this study, as one of the compounds in plant extracts, Tannin needs to know its ability to inhibit the corrosion rate of mild steel in the sulfuric acid solution. Previous research only measured the ability of at room temperature conditions, while this study using temperature variations to determine tannins' resistance as a bio inhibitor at different temperatures.

Its ability was tested using the weight loss method with variations in immersion time with different temperatures and inhibitor concentrations. This study's results can provide information about the best tannin ability to inhibit immersion time, temperature, and concentration.

2. METHODS

2.1 Preparing of Mild Steel

The material used in this study is mild steel with a composition (wt,%) 0.54Mn; 0.05Si; 0.01S; 0.01P; 0.16C, and the remaining is Fe. Mild steel cut into 30 x 20x 5mm size, cleaned using abrasive paper measuring 250# - 1000#. Then cleaned using acetone and rinsed using aqua dest and dried using a hot air blower then carried out the initial weighing.

2.2 Tannins Preparation

The tannins were TG 3300, the tannins in the form of powder were dissolved into aquadest with a concentration of 250; 500; 750; 1000; 1250 ppm.

2.3 Corrosive Medium

Corrosive medium used was 1M sulphuric acid with the immersion times were 2, 4, and 6 hours. Variation of concentration are 0; 250; 500; 750; 1000; 1250 ppm. Temperature used were 313K, 333K, and 353K.

2.4 Fourier-Transform Infrared Spectroscopy (FTIR) Analysis

We used Thermo Scientific Nicolet iSS FTIR Spectrometer to analyze the Tannin, which was tested in liquid form.

2.5 Weight Loss Measurement

Weight loss refers to the sample's different mass before and after being immersed in a corrosive medium. It was measured for various concentrations, temperatures, and times. From the data obtained, a corrosion rate was calculated, based on the weight loss using the formula (ASTM G31)(Fouda, Abousalem, & El- Ewady, 2017):

$$CR(mmpy) = (87500 \times \Delta W)/A\rho t \quad (1)$$

Where:

CR = corrosion rate

ΔW = weight loss (g)

A = the surface area in cm^2

P = the density of mild steel (g/cm^3)

t = immersion time (hr)

$$I.E\% = \left(\mathbf{1} - \frac{CR_{in}}{CR_{blank}}\right) x\ 100 \quad (2)$$

Where:

CR_{inh} = corrosion rates in the presence of inhibitor

CR_{blank} = corrosion rates in the absence of inhibitor

3. RESULT AND DISCUSSION

3.1 Characteristics of Tannins

Tannins are polyphenolic compounds that can work at poor pH conditions in the range of 0.5 - 4.0. The use of tannins at high pH is very rarely used. tannin compound used is TG 3300, a natural molecule with a density of 1.6 eq / Kg (dry basis).

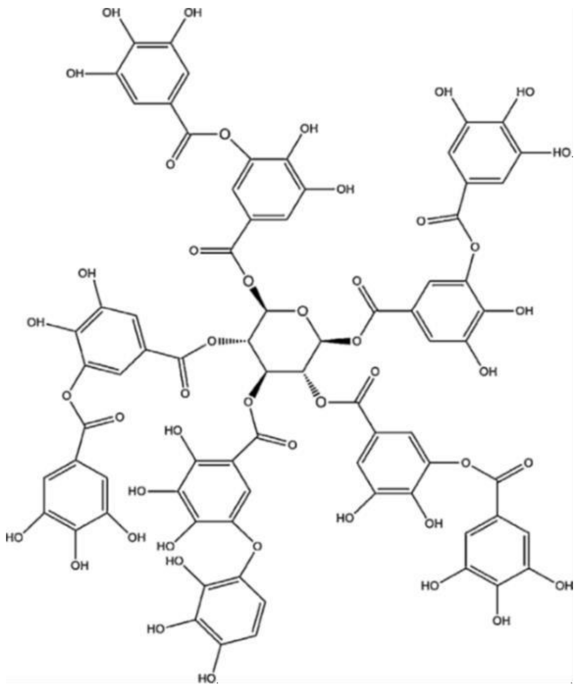

Fig. 1 Tannin's Chemical Structure

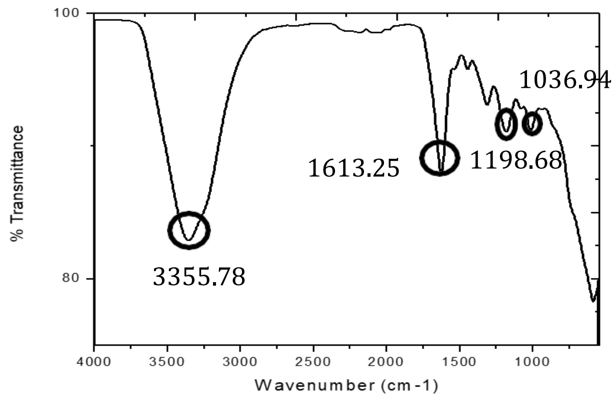

Fig. 2 Results of Tannin's FTIR Analysis

The functional groups that exist in tannins need to be characterized using FTIR. FTIR is an analysis carried out to identify functional groups present in tannins. The analysis results can be seen in Figure 2.

The typical spectrum of tannins is 1615 - 1606 cm^{-1} and 1452 - 1446 cm^{-1} (stretching vibration ring aromatic), 1211 - 1196 cm^{-1} and 1043 - 1030 cm^{-1} (stretching vibration with C-O bonds) and 1518 - 1507 cm^{-1} (stretching vibration ring aromatic)(Synytsya, Čopíková, Matějka, & Machovič, 2003).

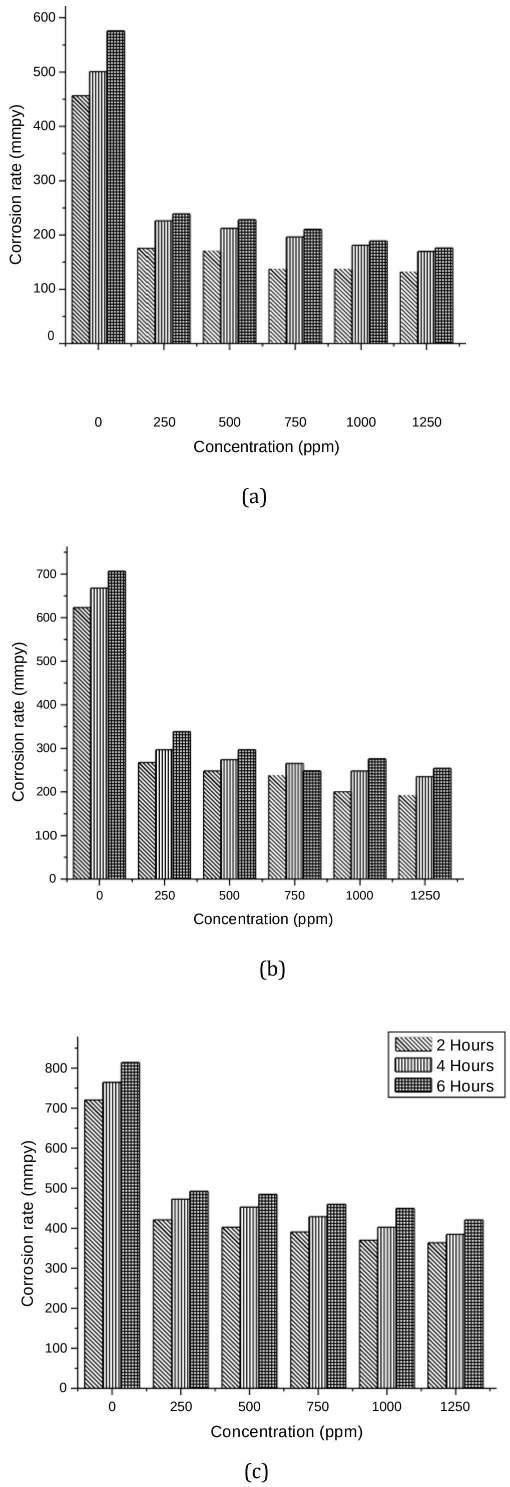

Fig. 3 Immersion Time and Inhibitor Concentration vs. Corrosion Rate at Temperature 313K (a), 333K (b), and 353K (c)

3.2 Effect of immersion time and tannin concentration on the corrosion rate

The immersion process was carried out for 2.4 and 6 hours at 313K, 333K, and 353K. Immersion was carried out to determine tannins' ability as bio-inhibitors in corrosive media with 1M H_2SO_4 solution at different temperatures. The results of the immersion process can be seen in Figure 3.

In Figure 3 as a whole, the corrosion rate increases with the length of immersion time at the same concentration. Immersion time causes the corrosion rate to decrease. The longer the immersion time, the less protective layer that has been formed due to the lengthy interaction with the corrosive media. More H^+ ions are formed so that the corrosion rate increases, as indicated by the increasing mass of mild steel, which decreases due to the more corrosive ions that attack the mild steel's surface.

Tannin contains an OH^- ions group in an ortho position on the aromatic ring to chelate with iron and other metal cations. Iron can be formed well because tannins are hydrolyzed. When Fe^{3+} ions react with OH^- ions in the ortho position, a blue-black complex of iron tannic solution is formed (Figure 4). The tannic will adhere to the metal surface, which will prevent further corrosion.

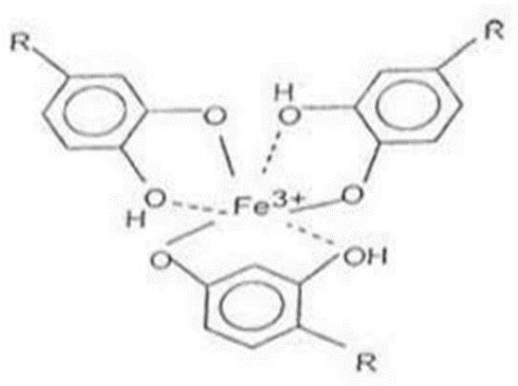

Fig. 4 Mechanism of Fe^{3+} chelate reactions (Cakar et ,al 2016)

3.3 Effect of immersion time and temperature on inhibition efficiency

The results of calculations using the weight-loss method, the efficiency values are shown in Table 1. The data presented in Table 1 shows the effect of temperature on the inhibition efficiency. Inhibition efficiency decreases with the increasing temperature of the corrosive medium. The higher the temperature, the more the reaction that occurs. As the temperature increases, the collisions between the reactants increase. In an acid medium (H_2SO_4), corrosion on the surface of mild steel is accompanied by hydrogen gas evolution.

The addition of inhibitor concentration can increase the efficiency value due to complex compounds in the inhibitor solution adsorbed on the mild steel surface to form a protective layer that can prevent corrosion attacks. The higher the tannin concentration, the more it will be adsorbed on the mild steel surface, increasing the inhibitor's efficiency inhibiting corrosion.

Table 1. The immersion time and temperature on inhibition efficiency

Temperature, K		Inhibition Efficiency, %					
		Inhibitor Concentration, ppm					
		0	250	500	750	1000	1250
	2 hrs	456.61	61.56	62.60	69.95	69.95	71.07
313	4	500.92	54.87	57.63	60.79	63.86	66.16
	6	575.7	58.54	60.40	63.52	67.17	69.45
	2	623.05	57.00	60.21	61.82	67.84	69.19
333	4	668.08	55.56	58.97	60.24	62.83	64.77
	6	706.69	52.09	57.95	60.01	60.96	64.04
	2	720.35	41.56	44.11	45.72	48.59	49.53
353	4	764.63	38.14	40.77	43.93	47.30	49.68
	6	813.89	39.51	40.44	43.51	44.74	48.36

The protection mechanism due to the reaction between Fe^{2+} and the inhibitor produces complex compounds(Peres, Cassel, & Azambuja, 2012). The reaction is as follows :

$$Fe \rightarrow Fe^{2+} + 2e \quad (1)$$
$$Fe^{2+} + 2e \rightarrow Fe \quad (2)$$
$$Fe^{2+} + Tannin \rightarrow [Fe(Tannin)]^{2+} \quad (3)$$

The complex compounds formed above have high enough stability. The theory that the efficiency of using an inhibitor depends on the stability of the chelating inhibitor molecule must have a nucleus capable of forming bonds with the metal surface through electron transfer.

4. CONCLUSION

The tannins' ability to inhibit corrosion in mild steel in 1 M sulfuric acid decreased with the length of immersion time and the increasing temperature. At the same immersion time and the same temperature, the inhibition efficiency increased with increasing tannin concentration. The highest inhibition efficiency was 71.07 % at a concentration of 1250 ppm, 313 K, and 2 hours of immersion.

5. ACKNOWLEDGEMENT

The authors are grateful to the Rekayasa Produk Kimia Alam (RPKA) Laboratory of Chemical Engineering Universitas Indonesia to support this work.

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