

## Influence of tannin content in *Terminalia catappa* leaves extracts resulted from maceration extraction on decreasing corrosion rate for mild steel in 1M H<sub>2</sub>SO<sub>4</sub>

M Pramudita<sup>1,2</sup>, Sukirno<sup>1</sup> and M Nasikin<sup>1</sup>

<sup>1</sup> Department of Chemical Engineering, Universitas Indonesia, Depok, 16424, Indonesia

<sup>2</sup> Department of Chemical Engineering, University of Sultan Ageng Tirtayasa, Banten, 42124, Indonesia

E-mail: mnasikin@che.ui.ac.id

**Abstract.** The ability of natural compounds as corrosion inhibitors is necessary to obtain safe corrosion inhibitors for the environment. The tannin compounds derived from plant extract has the ability to decrease the corrosion rate. The purpose of this research is to find the ability of tannin compounds in *Terminalia catappa* leaves extracts to decrease corrosion rate on mild steel. *Terminalia catappa* leaves that have been mashed in ethanol solvent extraction using maceration with the variable time 2.4 and 6 days. Mild steel that has been on the sandpaper and cleaned then soak into the 1 M H<sub>2</sub>SO<sub>4</sub>. *Terminalia catappa* leaves extract concentration used is 0, 250, 500, 500, 750, 1000 ppm, the immersion time is 3.6 and 9 hours. Calculating of corrosion rate is used the weight loss method, the analysis of the tannin concentration using GC-MS. The results indicate that highest tannin content equal to 7.23% in 6 days maceration time. The result showed that the corrosion rate was reduced in the presence of tannin content in *Terminalia catappa* leaves extract.

### 1. Introduction

Mild steel is defined as alloys of iron (Fe) and other alloying elements, such as Cr, Ni, and C, etc. Mild steel has been widely used as the material for fluid transmission pipes, such as gas, water, and oil. However, corrosion has been identified as the main problem of mild steel application.

Corrosion is degradation or deterioration of metals caused by a reaction of materials (commonly metals) with the environment [1]. Corrosion cannot be prevented or stopped and caused damage, especially in the industrial sector. Nevertheless, the addition of corrosion inhibitor is known as a suitable method to control metal corrosion [2].

Corrosion inhibitor is defined as a substance with the ability to decrease corrosion rate when added to an environment in a small concentration [3]. Inhibitor works by precipitating on the surface of protected metals and forming a thin layer that will protect metal from corrosion.

Corrosion inhibitor generally comes from the organic compound and anorganic, containing groups with free electron pairs such as nitrite, chromate, phosphate, urea phenylalanine, imidazoline, and amines compounds. However, synthetic chemicals are toxic and not environmentally friendly [4]. Hence, further research is needed to explore eco-friendly corrosion inhibitor, for instance, natural products inhibitor.



Recently, research regarding natural products as corrosion inhibitor has received much attention. Natural products are not only eco-friendly and ecologically acceptable but also renewable and available abundantly [5]. Natural products notably come from plant extract. Plant extract is renewable sources of materials, readily available and inexpensive. In addition, plant extract is biodegradable and free of both heavy metals and toxic substances [6].

Phytochemicals (i.e.: alkaloids, tannins, glycosides, saponins, flavonoids, polyphenol, etc.) exist abundantly in plant extract. Phytochemicals consist of N, O, P, S and atoms with free electron pair, which can be promoted as ligands that will form complexes with metals [7]. Those are organic compounds and contain heteroatoms in their molecules [8].

*Terminalia catappa* is plant extract that can be used to produce corrosion inhibitor. It has been reported *Terminalia catappa* leaves embodies several compounds used to inhibit corrosion rate, and tannin, which presents in the high content, is one of them [9].

Tannin is the high potential organic compound to be utilized as corrosion inhibitor. Tannin exhibits ability to form complexes with metals and able to work under low pH environment. In the previous studies regarding mimosa tannin successfully inhibits corrosion rate of steel, mechanism of oxide films stable chelates formation with Fe (III) has been reported [10]. Tannin is polyphenol compounds and usually found in plants with a large structure. These types of plants form macromolecule and contain the considerable amount of hydroxyl (-OH) groups. It is inferred that these groups enable tannin to form complexes with metals [11].

The extraction process was conducted in order to determine tannin content in *Terminalia catappa* leaves. Maceration is employed as extraction method in the present study. Maceration extraction is extraction using a cold solvent (without heating process). An advantage of this method is to minimize the possibility of thermolabile compounds damage. Thus, many compounds can be extracted [12].

Simplisia materials were ground and mixed with extraction materials and kept not exposed to direct light. Maceration durations are varied from 4 – 10 days. It is theoretically impossible for an absolute extraction to occur in maceration process since solvent will reach its saturation point. The high ratio of simplisia to extraction solution, more results can be obtained [13].

The present study is required in order to investigate the influence of tannin in *Terminalia catappa* leaves extract on corrosion rate inhibition. This study is expected to provide important findings for the advancement of *Terminalia catappa* leaves extract as a bio corrosion inhibitor.

## 2. Materials and methods

### 2.1. Materials

The material used in this study is mild steel with composition (% wt) : 0.54Mn, 0.05Si, 0.01S, 0.01P, 0.16C and the remaining Fe. Coupon (2.5 x 3 x 0.5 cm) were mechanically polished using grid 400# – 1200#, cleaned with acetone and dried. Afterwards, the coupon was weighed to determine initial weight [14].

### 2.2. Preparation of *Terminalia catappa* leaves extraction

*Terminalia catappa* leaves were obtained from University of Indonesia. Prior to maceration process, these leaves were dried, followed by size reduction using the blender. Maceration process was carried out with various duration (2, 4, and 6 days) and ethanol was used as a solvent.

### 2.3. Solutions

H<sub>2</sub>SO<sub>4</sub> 1M pa was simulated as corroding medium and corrosion inhibitor was applied in various concentration (0;250;500;750;1000 ppm). Immersion time was varied for 3, 5 and 9 hours [15].

#### 2.4. Weight Loss Technique and analysis

Weight loss technique was applied in the present study. Coupon initial and final weights were accurately weighted before and after immersion in the corrosive medium. From the obtained data, weight loss was determined, and the corrosion rate was calculated as follows [16]:

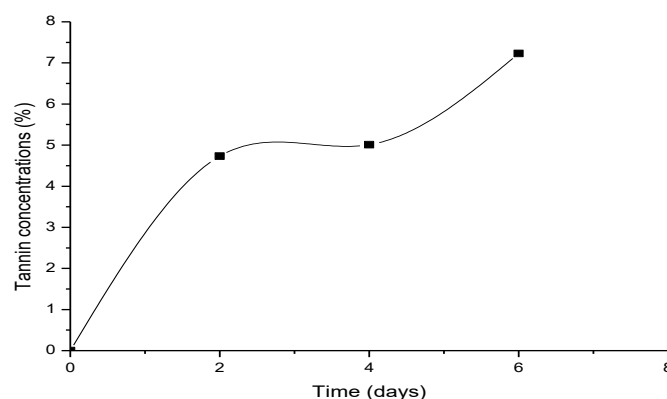
$$C_R (\text{mmpy}) = \frac{87600 \times \Delta W}{A \rho t} \quad (1)$$

where  $C_R$  is corrosion rate;  $\Delta W$  is weight loss (gram);  $A$  is coupon surface area ( $\text{cm}^2$ );  $\rho$  is the density of mild steel ( $\text{gram/cm}^3$ ) and  $t$  is immersion time (hours).

### 3. Result and Discussion

#### 3.1 Composition of tannin content in *Terminalia catappa* leaves in maceration extraction using ethanol as solvent

The influence of *Terminalia catappa* leaves extracts maceration extraction process on tannin content was investigated by various immersion time (2, 4 and 6 days). The GC-MS analysis was conducted in order to identify percentage tannin content from extraction maceration process. Figure 1 shows the relationship between tannin concentration and maceration time.



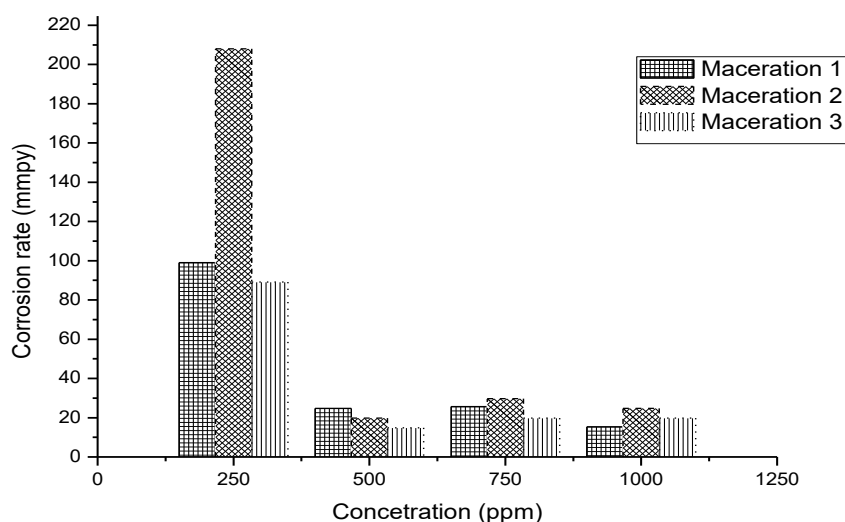
**Figure 1.** Graph plotting of tannin concentration in *Terminalia catappa* leaves extract vs maceration time.

From GC-MS analysis, tannin content percentages from immersion time of 2, 4 and 6 days in ethanol are 4.73%, 5.01%, and 7.23%, respectively. It is illustrated that the immersion time which obtained the highest tannin content (7.23%) was within 6 days. It is also inferred from Figure 1 that within 6 days, tannin concentration *Terminalia catappa* leaves extract was higher than 4 and 2 days. The ratio of *Terminalia catappa* leaves powder and ethanol were 1:4. Highest tannin content in maceration time of 6 days might be as a result of longer immersion time, which caused more tannin can be extracted from the process. However, it is theoretically impossible for an absolute extraction to occur in maceration process since solvent will reach its saturation point [15].

#### 3.2 Effect of inhibitor concentration on corrosion rate

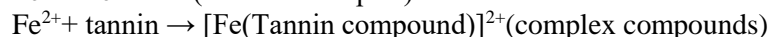
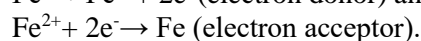
Corrosion rate was incited by addition of the inhibitor. Corrosion rates of mild steel decrease following the addition of inhibitor at a higher concentration, as depicted in Figure 2. Based on the amount of tannin in *Terminalia catappa* leaves extract, maceration 3 shows lower corrosion rate than maceration 1 and 2. Thus, tannin content in *Terminalia catappa* leaves extracts influenced corrosion

rate. In addition, there are several compounds – as impurities - along with tannin in *Terminalia catappa* leaves extract act as corrosion rate inhibitor.



**Figure 2.** Graph plotting of corrosion rate vs concentration in maceration time 1, 2, and 3.

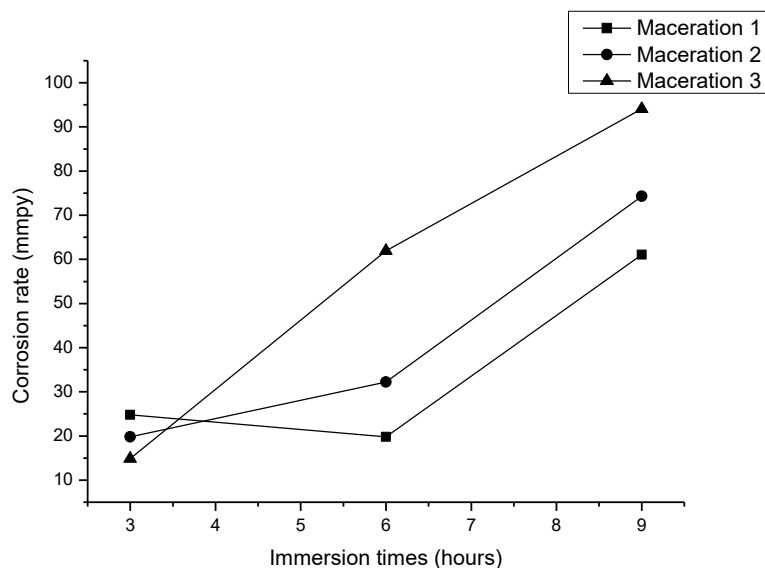
Addition of inhibitor at higher concentration corrosion rate might be originated from the presence of complex compounds (tannin compound) in inhibitor solution adsorbed on the surface of mild steel and form the protective layer. Hence, this layer plays the significant role in reducing corrosion attack within a short period of time. Corrosion rate reduced in the presence of tannin compounds is adsorbed on mild steel surface. Protection mechanism was carried out by reaction of  $\text{Fe}^{2+}$  and natural inhibitor results in the formation of complex compounds. Natural extract inhibitor which contains nitrogen act as an electron-pair donor to the surface of mild steel metal, whereas  $\text{Fe}^{2+}$  ion was diffused in the electrolyte solution, according to the following reaction scheme:



Complex compounds formed in the reaction above have high stability, and consequently, mild steel samples with natural extract inhibitor will exhibit high corrosion resistance [16]. This phenomenon is in agreement with theory, which states that efficiency of inhibitor relies on the stability of chelate formation and inhibitor molecules should be occupied with the ability of its core to bond with the metal surface through electron transfer [17].

### 3.3 Effect of mild steel immersion time in 1 M $\text{H}_2\text{SO}_4$ on corrosion rate

The relationship between immersion time and corrosion rate was plotted into the graph to observe the influence of immersion time on corrosion rate.



**Figure 3.** Graph plotting of corrosion rate as function of immersion time.

Figure 3 illustrates time maceration which gradually and cause to increase the rate of corrosion. This condition is a result of the longer interaction of mild steel surface with corroding medium  $H_2SO_4$ , which induced more corrosion occurs on the surface of mild steel due to  $H^+$  ion attack. Decreasing corrosion rate within 6 hours inhibition period was originated from the natural extract inhibitor addition to corroding medium. Natural extract inhibitor generated passive layer on the surface of mild steel, and optimally resisted attack from corrosive ions. On the other hand, longer inhibition period (9 hours) shows increasing corrosion rate. This results may be caused by a large amount of  $H^+$  ion was formed after interactions of the passive layer with corroding medium and accordingly, corrosion rate was increasing. It is evident with reduction of mild steel mass after inhibition process.

Furthermore, the passive layer of tannin-iron from *Terminalia catappa* leaves extract was unable to protect entire surface of steel, and consequently, unprotected parts can be ionized and experience corrosion. Corrosion rate was also influenced by accumulation of tannin impurities from *Terminalia catappa* leaves extract accumulated on the surface of the mild steel.

#### 4. Conclusion

The process of maceration extraction affects the amount of tannin content in *Terminalia catappa* leaves extract. The highest content of tannin during the six-day maceration period is 7.23%. From the results of corrosion rate testing showed that the higher the concentration of the inhibitor, the corrosion rate decreases. Time maceration which gradually and cause to increase the rate of corrosion.

#### References

- [1] Uhlig, Herbert H, Revie R and Winston 2008 *Corrosion and corrosion control* (New Jersey: John Wiley & sons, inc., Publication)
- [2] Kadhum A, Mohamad A, Hammed L, Al-Amiery A, San N and Musa A 2014 *Mater.* **7** (6) 4335-4348
- [3] NACE Glossary of Corrosion Terms 1965 *Mat. Pro.* **4** (1) 79-80
- [4] Umoren S A 2009 *Carbohydr. Polym.* **2** (1) 175-188
- [5] Tan K W and Kassim M J 2011 *Corros. Sci.* **53** (2) 569-574
- [6] Prabakaran M, Kim S H, Hemapriya V and Chung I M 2016 *J. Ind. Eng. Chem.* **37** 47-56
- [7] Ramji K, Cairns D R and Rajeswari, S 2008 *Appl. Surf. Sci.* **254** (15) 4483-4493
- [8] Zulfareen N, Kannan K, Venugopal T and Gnanavel S 2016 *Arab. J. Chem.* **9** (1) 121-135

- [9] Eddy N O, Ekwumemgbo P A and Mamza P a P 2009 *Green. Chem. Lett. Rev.* **2** (4) 223-231
- [10] Martinez S 2003 *Mater. Chem. Phys* **77** (1) 97-102
- [11] Zelinka S L and Stone D S 2011 *Mater. Corros* **62** (8) 739-744
- [12] Heinrich M B, Gibbons J, Williamsom S 2004 *Fundamentals of Pharmacognosy and Phytotherapy* (Philadelphia: Elsevier)
- [13] Voight R 1995 *Buku Pelajaran Teknologi Farmasi, diterjemahkan oleh Noerano Soendani* (Yogyakarta: Gajah Mada University Press) p. 56 159, 557
- [14] ASTM G 01-03 *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens.*
- [15] ASTM G 31-72 *Standard Practice for Laboratory Immersion Corrosion Testing of Metals.*
- [16] ASTM NACE/ASTMG31-12a, 2012, *Standard Guide for Laboratory Immersion Corrosion Testing of Metals*, ASTM International, West Conshohocken, PA
- [17] Martell, M C 1953 *Chemistry of Metal Chelate Compounds* (New York: Prentice Hall) p. 28-34
- [18] Slabbert N 1992 *Complexation of Condensed Tannins with Metal Ions*, ed R W Hemingway and P E Laks (New York: Plenum Press) p. 421-436