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The effect of mild steel immersion time on synergistic corrosion inhibitor ability of *terminalia catappa* leaves extract

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ABSTRACT

Inhibitors from natural materials are safe for the environment to replace chemical inhibitors in inhibiting corrosion. The tannin compounds contained in the *Terminalia Catappa* leaves extract have the ability to inhibit the corrosion rate. This study aims to determine the ability of *Terminalia Catappa* leaves extract and its synergism with KI in inhibiting the corrosion rate of mild steel metal. Mild steel that has been sanded and cleaned is then immersed in demineralized water. The immersion time was carried out in 3 variations which were 1, 3, and 5 hours. The weight-loss method is used to calculate the corrosion rate. The lowest corrosion rate was obtained at 0.0018 mmpy at immersion for an hour, and the concentration of inhibitor was 1250 ppm. The highest inhibition efficiency was obtained at 90% in immersion for an hour with a 1250 ppm inhibitor concentration.

ABSTRAK

Inhibitor dari bahan alam digunakan karena aman bagi lingkungan untuk menggantikan inhibitor bahan kimia dalam menghambat laju korosi. Senyawa tanin yang terkandung pada ekstrak daun ketapang memiliki kemampuan untuk menghambat laju korosi. Penelitian ini bertujuan untuk mengetahui kemampuan ekstrak daun ketapang dan sinergisitas dengan KI dalam menghambat laju korosi pada logam *mild steel*. *Mild steel* yang telah diamplas dan dibersihkan kemudian direndam ke dalam media korosif yaitu air demineralisasi. Waktu perendaman dilakukan pada 3 variasi waktu yaitu, 1, 3, dan 5 jam. Metode *weight loss* digunakan untuk menghitung laju korosi. Laju korosi terendah didapatkan sebesar 0.0018 mmpy pada perendaman selama 1 jam dan konsentrasi inhibitor 1250 ppm. Efisensi inhibisi tertinggi didapatkan sebesar 90% pada perendaman selama 1 jam dengan konsentrasi inhibitor 1250 ppm.

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1. Introduction

Corrosion is a process of decreasing metal quality due to an electrochemical reaction with its environment. Metals that experience corrosion does not only occur due to chemical reactions but can also occur due to electrochemical reactions. One of the factors that can cause corrosion of a material is the influence of the concentration of the corrosion medium [1]. Metal cannot be separated from the corrosion process destroying the metal, mainly when metal is used in underwater construction because the metal meets water and air, which causes the corrosion process to take place quickly. Several attempts to control the corrosion rate are selecting materials that can reduce the corrosion rate, coating metal surfaces to protect metals from corrosion, protecting the cathodic part, and using chemical substances commonly called inhibitors [2].

Corrosion inhibitors are substances that can reduce the rate of corrosion of metals. Inhibitors reduce the corrosion process by forming a thin layer, and there are also inhibitors influenced by the environment by the formation of deposits that protect the metal from corrosion processes that damage the metal [3]. Inhibitors are used to prevent corrosion. By forming a passive layer on the metal, and then blocking substances that cause corrosion of the metal. Corrosion inhibitors commonly used are chemical compounds containing sodium phosphate, nitrite compounds, chromates, etc. These compounds produce residues which, if continuously made, will result in buildup on the boiler walls so that corrosion occurs. In addition, the resulting residue can also endanger the environment and life. Therefore, inhibitors from natural ingredients are used to replace the inhibitors that produce these residues. Plant extracts were reported as corrosion inhibitors are rice husk extract [4], *Syzygium Jambos leaves* [5] *Sunflower seed hull extract* [6], *Sweet melon peel* [7], *Mangifera Indica peel* [8], *Eucalyptus plant leaf extract* [9], *Sida cordifolia* [10], *Walnut green husk* [11], *Black tea* [12], *Red onion seeds and peels* [13].

The use of plant extracts as corrosion inhibitors has recently been growing because of their abundance, renewability, and easy production. Based on phytochemical research, plant extracts contain alkaloids, flavonoids, polyphenols, glycosides and saponins [14]. These compounds have many heteroatom compounds and polar functional groups, which can improve the performance of mild steel in a corrosive environment [15].

Terminalia catappa leaves extract (TCLE) is one of the natural inhibitors that can reduce the corrosion rate. TCLE contains tannins which play a role in inhibiting the corrosion rate. Research on using TCLE as a corrosion inhibitor in H_2SO_4 1M showed that the inhibition efficiency decreased with the increasing temperature and immersion time. TCLE, which was used as a natural inhibitor, turned out to not be able to be used at high temperatures. It was because the inhibition efficiency of tannin compounds decreased with increasing temperature. Therefore, halide compounds must be synergized with tannins [16].

Research shows that halide ions can increase the efficiency of corrosion inhibitor inhibition. Halide ions (Cl^-, Br^-, I^-) have been shown to increase the efficiency of plant extract inhibition [17]. Kalium Iodide (KI) was chosen because iodine has the largest atomic radius in the halide group, so it is easily polarized. The use of KI is also to improve ion stabilization. In this study, it was found that the inhibition of tannins was more effective. In addition to the temperature factor, the immersion time factor is a consideration to determine the synergistic ability of TCLE-KI. Immersion time will be related to how long the strength of the inhibitor in inhibiting the corrosion rate of mild steel in its corrosive medium. This study aims to determine the effect of immersion time on the synergistic ability of tannins derived from TCLE with the addition of KI in demineralized water media.

2. Methods

2.1. Sample Preparation

Mild Steel samples were prepared with 25 x 30 x 5 mm dimensions. The compositions (wt%) of mild steel is used: 0.16C, 0.1P, 0.01S, 0.05Si, 0.54Mn and remaining portion was Fe. The sample was ground with a grinder and then cleaned with acetone (Merck 90%) to remove dirt on the surface of the mild steel sample. After being washed, dried, and weighed to get the initial weight before immersion.

2.2. Preparation of Terminalia catappa leaves extract

Terminalia catappa leaves were taken from the Faculty of Engineering, University of Sultan Ageng Tirtayasa, Cilegon Banten. At first, release the left blade from the *Terminalia catappa* leaves bone. Then smooth the leaves in a blender. After that, the maceration process was carried out by placing the results of the blender into a container and then adding ethanol as the extracting solvent. The maceration process lasted for four days stirring once a day. After the maceration process was complete, it was filtered with filter paper. Then the TCLE extract was separated with ethanol (Merck 70%) using a vacuum rotary evaporator. After that, TCLE was obtained, which would later be used as a corrosion inhibitor.

2.3. Corrosion Inhibition Process

Prepare demineralized water media and inhibitors of TCLE with concentrations of 0, 250, 500, 750, 1000, and 1250 ppm and KI (Sigma Aldrich 99%) with a concentration of 50 ppm. The mild steel sample was immersed in demineralized water media, inhibitor, and KI. Immersion time for 1, 3, and 5 hours and variations in temperature 30℃, 50℃, and 70℃. Then the mild steel sample was washed with acetone and weighed for data collection after immersion.

2.4. Weight-Loss Methods

Weight loss is a method for determining weight loss value after immersion at a particular time. The weight-loss method is used because the equipment used is not complicated and accurate. The weight-loss method determines the corrosion rate by determining the amount of material weight lost after the material is soaked with the ASTM G31-72 standard. The equation can determine the corrosion rate:

$$Cr = \frac{87500 \times \Delta W}{\rho \times A \times \Delta t}, \quad (1)$$

where Cr is corrosion rate (mmpy), ΔW is the weight loss (g), ρ is the density of mild steel (g/cm^3), A is the sample area (cm^2), and Δt is the immersion times (hours). The percentage of inhibition efficiency (IE%) is calculated using the following equation:

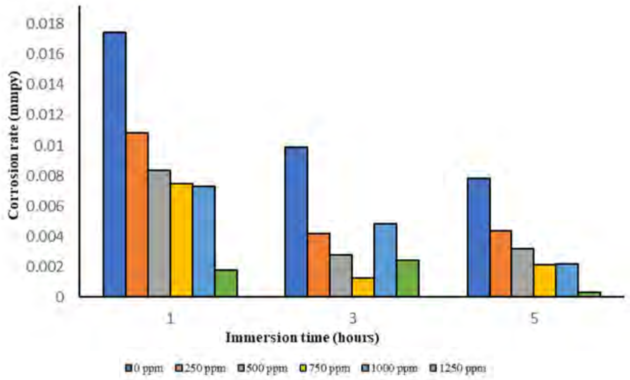
$$\%IE = \left(1 - \frac{Cr_{inh}}{Cr_o}\right) \times 100\%, \quad (2)$$

where Cr_{inh} is corrosion rate with inhibitor (mmpy) and Cr_0 is corrosion rate without inhibitor (mmpy).

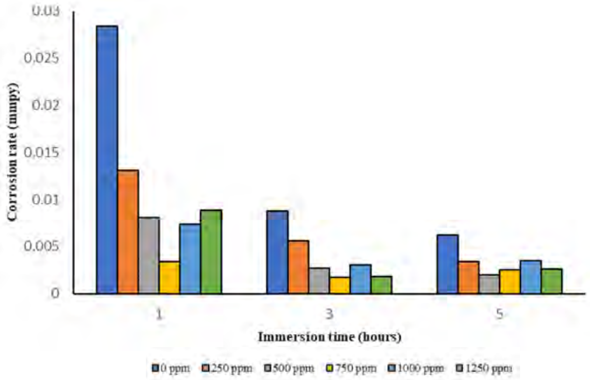
3. Result and Discussion

3.1. Effect of Immersion Time and Concentration on Corrosion Rate

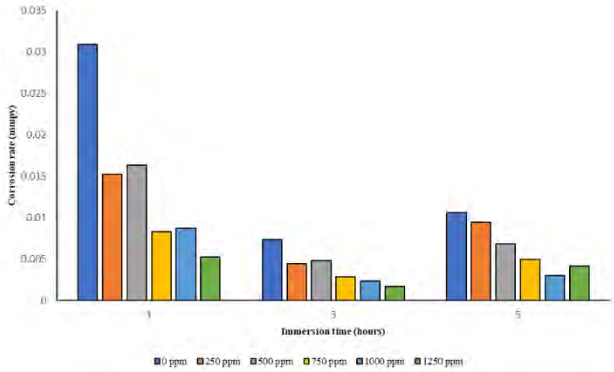
This study uses variations in the concentration of TCLE of 0 ppm, 250 ppm, 750 ppm, 1000 ppm, and 1250 ppm with variations in immersion temperature of 30℃, 50℃, and 70℃ and immersion time for 1 hour, 3 hours, and 5 hours. The results of immersion with variations in time and concentration of the TCLE can reduce the corrosion rate. The graph of the effect of immersion time on the corrosion rate can be seen in Figure 1.



(a)



(b)



(c)

Figure 1. Immersion time and concentration on corrosion rate at (a) T= 30ºC, (b) T = 50ºC, and (c) T = 70ºC.

Figure 1 shows that with increasing inhibitor concentration, the corrosion rate decreases. It happens because the higher the inhibitor concentration, the more inhibitor content to protect the mild steel sample. The higher the inhibitor concentration, the more tannin content forms complex compounds with corrosive agents and covers the surface of the mild steel sample so that the corrosion process is hampered. This layer cannot be seen directly but can inhibit the corrosion process of mild steel. Tannins from TCLE, which react with demineralized water, will show the formation of a protective layer that covers the surface of the mild steel electrode, where the layer will form a film so that it can inhibit the corrosion process. Then, water molecules and other ions are initially adsorbed on the mild steel surface and then removed by tannins. The thickness of this protective layer increases with the concentration of tannins in the TCLE because more and more tannins are electrostatically adsorbed on the mild steel surface, which results in a decrease in the capacitance value. Thus, a barrier layer that can be formed on the surface of mild steel in various immersion times and concentrations of the inhibitor can prevent the mild steel from corrosion.

Tannins contain OH^- groups in the ortho position on the aromatic ring so that they can form chelates with iron and other metal cations. Iron tannates can be formed well because the tannins are hydrolyzed. Iron tannate complex solution is formed when Fe^{3+} ions react with OH^- in the ortho position. Tanat will be attached to the iron surface to prevent further corrosion [18]. The effect of concentration on the corrosion rate indicates corrosion inhibition due to the increase in tannins in the concentration of inhibitors of TCLE. It is caused by the adsorption of inhibitors on the electrodes on the mild steel surface. High inhibitors indicate that tannins can inhibit the reduction of hydrogen ions in the cathodic portion of mild steel [19].

In Figures 1(a), 1(b), and 1(c), the corrosion rate increases with increasing immersion temperature. It happens because the higher the temperature, the kinetic energy of the reacting particles increases, thus affecting the magnitude of the activation energy. The speed of the corrosion rate will be higher when the kinetic energy of the reaction is greater than the activation energy and the easier it is for corrosion reactions to occur in mild steel samples [20]. With the increase in temperature in the demineralized water media, the particles in the demineralized water media more often react with one another, so the corrosion formation reaction will be more straightforward. The higher the temperature, the lower the viscosity of the demineralized water media, making it easier for oxygen to diffuse to the surface of the mild steel sample. It will increase the corrosion rate in the mild steel sample because the amount of dissolved oxygen is mainly consumed in the reduction process at the cathode region [21].

TCLE will react with Fe^{2+} generated on the mild steel surface, forming a Fe-inhibitor complex:

$$Fe \longrightarrow Fe^{2+} + 2e$$

$$Fe^{2+} + TCLE_{(ads)} \longrightarrow [Fe\text{-}TCLE]^{2+}_{(ads)}$$

The complex compounds formed will be adsorbed on the surface of the mild steel and reduce the solubility of mild steel in demineralized water. The mechanism of inhibition of I- ions can replace hydroxyl ions that are adsorbed on the surface of mild steel because I- ions have more significant ionic properties, high hydrophobicity, and low electronegativity, which can reduce the catalytic effect of hydroxyl ions [22].

$$Fe + H_2O + I^- \longrightarrow [FeIOH]^-_{ads} + H^+ + e$$

$$[FeIOH]^-_{ads} \longrightarrow FeIOH + e$$

$$FeIOH + H^+ \longrightarrow Fe^{2+} + I^- + H_2O$$

In addition, the presence of I^- supports the formation of ion pairs with organic inhibitor cations. The appearance of ion pairs is caused by the adsorption of I^- on the mild steel surface, leading to a bridge between the metal surface and the inhibitor.

3.2. Effect of Immersion Time and Inhibitor Concentration on Inhibition Efficiency

The effect of immersion time on the efficiency of inhibition indicates that the higher the concentration of the inhibitor used, the higher the efficiency of the inhibitor will be. It is because the more significant the concentration of the inhibitor, the more adsorption processes that form a protective layer with the tannin complex, so that the corrosion rate can be reduced, and the efficiency of the inhibitor used is increased. The experimental data and calculations can be seen in table 1.

Table 1 shows that the higher the inhibitor concentration, the better the inhibition efficiency. Inhibition efficiency indicates the ability of the inhibitor to inhibit the corrosion rate. The higher the concentration of the inhibitor, the better the inhibitor in inhibiting the corrosion rate. The longer the immersion time, the inhibition efficiency of mild steel will decrease, this is because the sample reacts with demineralized water. The complex compound formed by the inhibitor forms a very thin passivation layer on the mild steel surface to protect the mild steel surface. the highest inhibition efficiency was at 1 hour immersion time with a concentration of 1250 ppm. The longer the immersion time causes the passivation layer that is formed to start to break down so that the corrosion process takes place [14]. The shorter the contact time between the metal and the corrosive media and the inhibitor, the work of the inhibitor will be maximized because the value of the inhibition efficiency will increase.

Table 1. Immersion time and inhibitor concentration on inhibition efficiency.

Time immersion (hours)	**Temperature ^oC**	**Inhibition efficiency (%)**				
		Concentration (ppm)				
		250	**500**	**750**	**1000**	**1250**
1	30	38	52	57	58	90
3		57	72	87	51	76
5		45	59	73	72	66
1	50	54	71	88	74	69
3		36	69	81	65	80
5		46	69	61	44	58
1	70	51	47	73	72	83
3		39	34	62	68	76
5		12	36	54	72	61

The ability to inhibit a metal is measured by its efficiency. The efficiency value depends on the concentration of the inhibitor used. Based on table 1, at the same immersion time, the inhibition efficiency value produced from the TCLE will increase along with the increase in the concentration of the bio inhibitor to reduce the corrosion rate. The higher the added concentration affects the efficiency of the inhibition. The higher the concentration, the better the adsorption process and the inhibitor's formation of a protective layer. The appearance of a protective layer results from the interaction of nano silicate molecules with the atoms of the mild steel base surface [23]. It is because more and more protective layers are formed to prevent corrosion from being absorbed maximally and adequately on the mild steel surface. With the higher inhibitor concentration added, the protective effect becomes more maximal. The classification of corrosion inhibitors based on the efficiency of inhibition is bad if the value of inhibition efficiency is (<40% EI), quite good (40-69% EI) and very good (>70% EI) [22]. It can be seen from Table 1 that in use, the average efficiency of inhibition is more than 40%, so the corrosion inhibitor can be said to work quite well.

4. Conclusion

The greater the concentration of inhibitors used; the corrosion rate will decrease. The lowest corrosion rate was obtained at the addition of a concentration of 1250 ppm of 0.0018 mmpy with an immersion time of 1 hour. The most excellent inhibition efficiency was received at the addition of a concentration of 1250 ppm TLCE by 90% for 1 hour of immersion. At the same concentration, the longer the immersion time, the higher the corrosion rate and the lower the inhibition efficiency.

REFERENCES

[1] Yanuar, A. P., Pratikno, H., & Titah, H. S. (2016). Pengaruh penambahan inhibitor alami terhadap laju korosi pada material pipa dalam larutan air laut buatan. *Jurnal Teknik Institut Teknologi 10 November, Vol 5, No. 2.*

[2] Fontana, Mars Guy. (1987). *Corrosion Engineering* (3rd Ed.). Singapore: McGraw-Hill Book Co.

[3] Han, P., He, Y., Chen, C., Yu, H., Liu, F., Ma, Y., & Zhang, Y. (2016). Study on synergistic mechanism of inhibitor mixture based on electron transfer behaviour. *Scientific Reports vol.6 (September) 1-10.*

[4] Pramudita, M., Nasikin, M., & Sukirno. (2019). Synergistic corrosion inhibition effect of rice husk extract and KI for mild steel in H_2SO_4 Solutions. *Bulletin of chemical reaction engineering and catalysis, 14(3) 697 – 704.*

[5] Bangera, S., Alva V. D. P. (2020). Corrosion inhibitive property of environmentally Benign Syzygium Jambos Leaf Extract on mild steel in 1 M HCl. *Journal of Failure Analysis Previous, 20(3):734–743.*

[6] Hassannejad, H., & Nouri, A. (2018). Sunflower seed hull extract as a novel green corrosion inhibitor for mild steel in HCl solution. *Journal of Molecule Liquid, 254:377–382.*

[7] Saeed, M. T., Saleem, M., Usmani, S., Malik, I. A., Al-Shammari, F. A., & Deen, K. M. (2019). Corrosion inhibition of mild steel in 1 M HCl by sweet melon peel extract. *Journal of King Saud Univ Science, 31(4):1344–135.*

[8] Ogunleye, O. O., Eletta, O. A., Arinkoola, A. O., & Agbede, O. O. (2018). Gravimetric and quantitative surface morphological studies of Mangifera indica peel extract as a corrosion inhibitor for mild steel in 1 M HCl solution. *Asia Pacific Journal Chemical Engineering, 13(6): e2257.*

[9] Abdel-Gaber, A. M., Rahal, H. T., & Beqai, F. T. (2020). Eucalyptus leaf extract as an eco-friendly corrosion inhibitor for mild steel in sulfuric and phosphoric acid solutions. *International Journal of Industrial Chemical, 11(2):123–132.*

[10] Saxena, A., Prasad, D., Haldhar, R., Singh, G., & Kumar, A. (2018). Use of Sida cordifolia extract as green corrosion inhibitor for mild steel in 0.5 M H2SO4. *Journal of Environmental Chemical Engineering, 6(1):694–700.*

[11] Li, X., Deng, S., Du, G., & Xie, X. (2020). Synergistic inhibition effect of walnut green husk extract and sodium lignosulfonate on the corrosion of cold-rolled steel in phosphoric acid solution. *Journal Taiwan Instrumentation of Chemical Engineering, 114:263–283*.

[12] Verma, D. K, & Khan, F. (2015). Corrosion inhibition of high carbon steel in phosphoric acid solution by extract of black tea. *Advances in research. 1–9*.

[13] Noor, E. A., Al-Moubaraki, A., Al-Zhrani, A. H., & Hubani, M. H. (2016). Testing and comparing the inhibitory action of red onion seeds and peels extracts on the corrosion of steel in phosphoric acid. *International Journal of Electrochemical Science, 11:6523–6539.*

[14] Pramudita, M., Nasikin, M., & Sukirno. (2018). Rice husk extract ability to reduce the corrosion rate of mild steel. *International of chemical engineering applications, 9: 143 -146.*

[15] Chaubey, N., Qurashi, A., Chauhan, D. S., Quraishi, M. (2021). Frontiers and advances in green and sustainable inhibitors for corrosion applications: A critical review. *Journal of Molecule Liquid, 321:114385.*

[16] Pramudita, M., Sukirno, & Nasikin, M. (2020). Performance of Terminalia catappa leaves extract as a bio-corrosion inhibitor for mild steel in H2SO4 Solutions. *Proceeding of the 9th Annual International Conference (AIC) Banda Aceh, Indonesia. IOP Conf. Ser.: Mater. Sci. Eng.* **796** 012059. Doi:10.1088/1757-899X/796/1/012059.

[17] Umoren, S. A., & Solomon, M. M. (2017). Synergistic corrosion inhibition effect of metal cations and mixtures of organic compounds: A Revi*ew. Journal of Environmental Chemical Engineering, 5(1): 246-273.*

[18] Peres, Rafael Silveira., Cassel, Eduardo., & Azambuja, Denise Schermann. (2012). Black Wattle Tannin As Steel Corrosion Inhibitor. *International Scholary Research Network, ISRN Corrosion Volume 2012, Article ID 937920, 9 pages.*

[19] Peres, R. S., Cassel, E., & Azambuja, D. S. (2012). Black wattle tannin as steel corrosion inhibitor. *International Scholarly Research Notices*, vol. 2012, Article ID 937920, 9 pages, https://doi.org/10.5402/2012/937920.

[20] Xu, W., Han, E-H., & Wang, Z. (2019). Effect of tannic acid on corrosion behaviour of carbon steel in NaCl solution. *Journal of Materials Science Technology, 35(1):64–75.*

[21] Miralrio, A., & Espinoza, V. A. (2020) Plant extracts as green corrosion inhibitors for different metal surfaces and corrosive media: A review. *Processes 8(8):942.*

[22] Sundjono, S., & Saefudin, S. (2018). Pengaruh temperatur dan pH air sadah Kalsium Sulfat terhadap korosi pada baja karbon. *Metalurgi, 29*(*1*)*, 41-50.*

[23] Umoren, S. A., Solomon, M. M. (2015). Effect of halide ions on the corrosion inhibition efficiency of different organic species – A review. *Journal of Industrial and Engineering Chemistry, 21: 81-100.*

[24] Awizar, D. A., Othman, N. K., Jalar, A., Daud, A. R., Rahman, I. A., & Al-hardan, N. H. (2013). Nano silicate Extraction from Rice Husk Ash as Green Corrosion Inhibitor. *International Journal of Electrochemical Science., 8 (2013) 1759 – 1769.*