Jurnal Akademika Kimia, 10(3): 153-158, August 2021
ISSN (online) 2477-5185 | ISSN (print) 2302-6030
http://jurnal.fkip.untad.ac.id/index.php/jak/

Concentration Effect of Watermelon Skin Extracts (Albedo) as Organic Inhibitors on the Corrosion of Iron Nails in 3% NaCl Medium Solution

Nurhikmah & *Minarni R. Jura
Program Studi Pendidikan Kimia/FKIP – Universitas Tadulako, Palu – Indonesia 94119

Received 14 May 2021, Revised 30 June 2021, Accepted 09 August 2021
doi: 10.22487/j24775185.2021.v10.i3.pp153-158

Abstract

This study aimed to compare the concentration effect of skin extract in watermelon on the inhibition of corrosion rates of iron nails in the corrosive medium of NaCl solution and seawater. The study began with the first maceration of the skin in watermelon and then followed by evaporation to produce extracts specific gravity 0,097 gram/mL as inhibitors with variations in concentrations of 1,2,4,8 and 16%. Determining the corrosion rate used was the weight loss method from the 7-day immersion process. The results showed that the most excellent corrosion inhibition efficiency occurred at a concentration of 8% for immersion with 3% NaCl corrosive medium and 4% concentration for immersion in seawater with the efficiency of 11.56% and 22.15%, respectively. Based on the study results, it was found that each addition of extract in watermelon can affect the effectiveness of inhibition.

Keywords: Watermelon skin, iron nails, corrosive medium, corrosion rate, inhibition efficiency

Introduction

The development of technology, economic growth, and increasing activity have made some community activities inseparable from using various metals, such as iron, steel, aluminum, silver, and others. It uses these metals in multiple industries, both principal and additional components. Still, the obstacle is the occurrence of corrosion or rusting of the metal. Corrosion is one of the factors that cause the usability of the metal itself to decrease (Irianty & Khairat, 2013).

Seawater conditions are one of the environments that can accelerate the corrosion of a metal. Because seawater is one of the environments with a high level of corrosivity, it is necessary to apply corrosion rate control in the seawater environment. NaCl salt solution is a salt that can be used as a corrosive test environment in laboratory experiments to simulate seawater conditions. The concentration of NaCl solution in seawater also ranges from 3-3.5%, but the content of other ions such as Ca^{2+} and Mg^{2+} in natural seawater can form a layer of $CaCO_3$ and $Mg(OH)_2$ on the metal surface. So that in some experiments, a 3-3.5% NaCl solution was used as artificial seawater (Gunaatmaja, 2011).

Corrosion is a problem that is always faced because corrosion of a metal cannot be avoided or stopped. Still, its rate can be controlled or slowed down to reduce losses and prevent negative impacts, such as coating the metal surface, cathodic protection, adding inhibitors, corrosion, and others. Based on these various methods, the use of inhibitors is one of the effective ways to prevent corrosion because the cost is relatively cheap, and the process is simple. Both synthetic and natural, Corrosion inhibitors are divided into two major parts, namely inorganic inhibitors and organic inhibitors (Ilim et al., 2007).

Corrosion can occur through redox reactions, where iron is oxidized while oxygen is reduced. Rust is generally in oxides or carbonates; rust on iron is a reddish-brown substance with $Fe_2O_3.xH_2O$. Iron oxide (rust) can peel off so that the newly exposed surface gradually corrodes (Ahammed, 1998). In general, the corrosion mechanism in a solution begins with the metal being oxidized and releasing electrons to form positively charged metal ions. The solution will act as a cathode, with a common reaction being the release of H_2 and the reduction of O_2 due to the reduced H^+ and H_2O ions. This reaction occurs on the metal surface, which will cause peeling due to the dissolving of the metal into the solution repeatedly (Nurdin & Syahri, 1999).

A corrosion inhibitor is defined as a substance that reduces the rate of environmental corrosion of metals when added in small amounts to the environment. Generally, corrosion inhibitors come from organic and inorganic compounds containing

*Correspondence:
Minarni Rama Jura
e-mail: minarni.ramajura@gmail.com

groups that have lone pairs of electrons, such as nitrite, chromate, phosphate, urea, phenylalanine, and amine compounds that are hazardous and not environmentally friendly. Corrosion inhibitors from organic and inorganic compounds can be replaced with inhibitors from natural extracts that are environmentally friendly (Irianty & Khairat, 2013).

Corrosion inhibitors generally come from organic and inorganic compounds. Inorganic compounds, nitrite, chromate, phosphate, and urea, are used. These compounds are dangerous, expensive, not environmentally friendly because their toxic properties can cause temporary or permanent damage to organ systems of living things, such as disorders of the kidneys, liver, and enzyme systems. Organic compounds used as inhibitors can work as cathodic, anodic, or together through the surface adsorption process by forming a film layer. This inhibitor builds a hydrophobic film that protects the metal surface, thus preventing metal destruction in the electrolyte solution (Dariva & Galio, 2014). Inhibitors from natural extracts are a safe and appropriate solution because they are easy to obtain, biodegradable, low cost, and environmentally friendly. Extracts of natural ingredients, especially compounds containing N, O, P, S atoms, and atoms that have lone pairs of electrons so that they can form complex compounds with metals (Hosary et al., 1972). Elements that contain lone pairs of electrons can later function as ligands that include tough compounds with metals. The inhibitor is adsorbed on the metal surface and forms a thin film with a thickness of several inhibitor molecules. This layer is invisible to the naked eye but can inhibit environmental attacks on metals. The effectiveness of natural extracts as corrosion inhibitors cannot be separated from the nitrogen content contained in their chemical compounds (Prihandani et al., 2016).

Watermelon is a plant that grows in soil rich in organic matter content, fertile, loose, and has good aeration and drainage. This plant is an annual plant whose life is vines and has various species such as red watermelon, yellow watermelon, seed watermelon, and non-seeded watermelon. Watermelon (Citrullus lanatus) is a plant originating from Africa. It is one of Indonesia's most famous horticultural plants because of its sweet taste, high water content, and crunchy texture (Widyastuti et al., 1993).

Watermelon has a unique appeal; watermelon flesh is low in calories and contains 93.4% water, 0.5% protein, 5.3% carbohydrates, 0.1% fat, 0.2% fiber, and vitamins (A, B, and C) with a vitamin C content of 6 mg per 100 grams of material. It also contains the amino acid citrulline ($C_6H_{13}N_3O_3$), acetic amino acid, malic acid, phosphoric acid, arginine betaine, lycopene, carotene, bromine, sodium, potassium, sylvite, lysine, fructose, dextrose, and sucrose. In the flesh and skin of watermelon found substance L-citrulline. L-citrulline is more commonly found in the skin in watermelon, which is about 60% (Wu et al., 2007).

L-citrulline is an organic compound containing amide, carboxyl, and amine groups in non-essential amino acids. This compound is the leading natural ingredient in all parts of the watermelon (Citrullus Lantanus). Research on the corrosion inhibition properties of L-citrulline compounds has been carried out; it is known that L-citrulline can act as a corrosion inhibitor in mild steel. L-citrulline can inhibit the corrosion rate, increasing the efficiency of inhibition along with the increase in the concentration of L-citrulline (Odewunmi et al., 2015).

This paper aims to describe the ability of watermelon rind extract to affect the corrosion rate of iron nails and the effect of the concentration of watermelon rind extract as a corrosion inhibitor.

Methods

The tools used are measuring flask, blender, 40 mesh sieve, desiccator, measuring cup, watch glass, dropper, beaker, oven, analytical balance, spatula, evaporator, shaker, tube clamp, and stirring rod. The materials used are watermelon rind, 4-inch iron nails, filter paper, sandpaper, 3% NaCl, 0.1 M $NaHCO_3$, 96% ethanol, rust cleaning fluid, 1% $FeCl_3$, distilled water, seawater, and aluminum foil.

Sampling method

The sample of iron nails used by purposive sampling technique or researchers determines the characteristics of the sample to be used, namely with a size of 10.16 cm as many as 12 pieces. For inhibitors, watermelon rind extract is used, containing L-citrulline, reducing the corrosion rate. The rind in the watermelon used in this study was obtained from a fruit seller in the impressed market of West Palu, Central Sulawesi. The watermelon is cut into two parts and then separated from the skin and flesh, then split the inner skin of the watermelon and the outer skin of the watermelon so that the white skin of the watermelon is obtained (Zakaria et al., 2016).

Preparation of peel powder in watermelon

The procedure for preparing the peel powder in watermelon follows the research procedure of Tandjaja (2013). Watermelon is taken from the inner skin and cut into smaller pieces. They are then dried in the oven for 6 hours at a temperature of 50 °C. After that, the rind in the dried watermelon was blended to obtain a coarse powder of the skin in the watermelon and sieved with a size of 4 mesh to get the rind powder in the watermelon.

Twelve iron nails with an average dimension of 10 cm and a diameter of 0.5 mm were weighed, each 5 for treatment with the addition of various inhibitors and 1 without the addition of inhibitors for both 3% NaCl immersion and seawater. The nail's surface was smoothed with sandpaper and then soaked with 0.1 M sodium hydrogen carbonate. Next, the nail was dried in an oven at 100 °C for 20 minutes. Then cooled in a desiccator for 10 minutes and weighed (W_0) (Arenas et al., 2002).

Preparation of inhibitor solution (extraction)

This extraction procedure follows the research procedure (Purnomo & Sumarji, 2015). The peel powder in the watermelon was weighed as equates 100 grams and then put into a beaker; 500 mL absolute ethanol was added. Then the mixture was macerated and left in a beaker for 72 hours; the maceration results were filtered using filter paper. Then the filtrate was put into a round bottom flask, then evaporated at a temperature of 50-60 °C for 1 hour. The concentrated extract obtained was made in 5 different concentrations of 1%, 2%, 4%, 8%, and 16%.

Qualitative analysis

This qualitative analysis procedure follows the procedure of a study on the efficiency of corrosion inhibition in steel using mangosteen peel (Nasution et al., 2012). 10 grams of skin extract in watermelon is put into a beaker, then 10 mL of distilled water is added and heated until boiling. After that, it was filtered, and the filtrate was taken, then 10 drops of 1% $FeCl_3$ were added to the filtrate. $FeCl_3$ is used to determine whether the sample contains antioxidants indicated by a dark green color after being added with $FeCl_3$; a dark green color gives a positive result (Harborne, 1996).

Immersion of nails in corrosion medium

The immersion of nail samples was carried out in 2 ways: immersion without adding inhibitor and immersion with inhibitor solution with varying concentrations of 1%, 2%, 4%, 8%, and 16%. As for the test environment or corrosive medium uses sodium chloride (NaCl) with a concentration of 3% (artificial seawater) and natural seawater to compare the corrosion rate. The 3% NaCl corrosive medium was prepared using the dilution method, namely 3 grams of solid NaCl added 100 mL of distilled water. Natural seawater is taken from the sea around the Talise Beach Pavilion, Palu, Central Sulawesi. Immersion of nails in this corrosive medium followed the research procedure (Sari et al., 2013).

Determination of corrosion rate

The tests were carried out using the weight-loss method, which refers to the ASTM GI standard with the calculation of the corrosion rate using the following equation (Poursaee, 2011)

$$Corrosion\ Rate = \frac{3.45\ x\ 10^6 . W}{A.T.D}$$

Where Corrosion rate in Mpy; W is the mass lost (grams); D is the density of the specimen (gram/mL); the surface area of the specimen (cm^2), and T is the immersion time (hours).

Determination of inhibition efficiency

The determination of the inhibition efficiency in this study was calculated by the formula of the Tafel extrapolation method as follows (Abdurahman, 2010).

$$Inhibition\ efficiency = \frac{Cr_a - Cr_b}{Cr_a}\ x\ \ 100\%$$

Cr_aa is the corrosion rate without rind extract in watermelon, and Cr_b is the corrosion rate with rind extract in watermelon.

Results and Discussion

Citrulline qualitative analysis

The qualitative analysis carried out in this study aimed to determine the presence of the chemical compound citrulline in the peel extract in watermelon, which can slow down the corrosion rate of metals. Phytochemical analysis was carried out in this study, namely adding extract with 1% $FeCl_3$ reagent indicated by the color change. A phytochemical test using $FeCl_3$ is used to determine whether the sample contains antioxidants characterized by a dark green color. After adding $FeCl_3$, the dark green color gives a positive result.

Nail corrosion rate

The corrosion rate is the metal released per unit on a specific surface. The unit of corrosion rate is generally expressed in mils per year (mpy). In testing the corrosion rate of iron nails in 3% NaCl solution medium and seawater with an immersion time of 168 hours, it was seen that there was a difference between the added iron nail sample and without the addition of inhibitor solution of peel extract in watermelon both in 3% NaCl medium and in medium seawater.

Based on the research results, the addition of watermelon rind (Albedo) can affect the rate of corrosion reaction in iron raw both in NaCl medium and in seawater medium. It is due to the presence of Citrulline compounds present in the extract. Citrulline compounds in the extract can form complex compounds with Fe(II) on metal surfaces (Favre & Landolt, 1993). So that there is a decrease in the corrosion rate in the 3% NaCl medium from the addition of inhibitors with a concentration of 1% and 8%. The Fe(II) complex compound will be attacked by corrosive ions on the metal surface so that the corrosion reaction rate will decrease. However, there was an increase in the corrosion rate with an inhibitor with a concentration of 16%. However, it was different in seawater medium, where there was a decrease in the corrosion rate with the addition of inhibitors at 1% and 4% concentrations. It again increased at 2%, 8%, and 16% concentrations. The Fe-citrulline extract layer cannot cover the entire nail's surface, so the parts not covered with Fe can be ionized and corroded. In addition, there are impurities in the citrulline extract compound attached to the steel surface which also affects the speed of corrosion (Wahyuni, & Syamsudin, 2014).

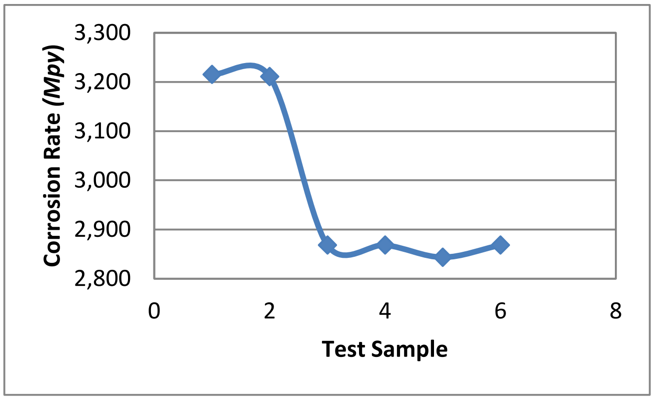

Figure 1. Graph of effect without addition of inhibitor (Paku1) and addition of inhibitor (Paku 2-6) of watermelon rind extract on iron spikes in 3% NaCl medium

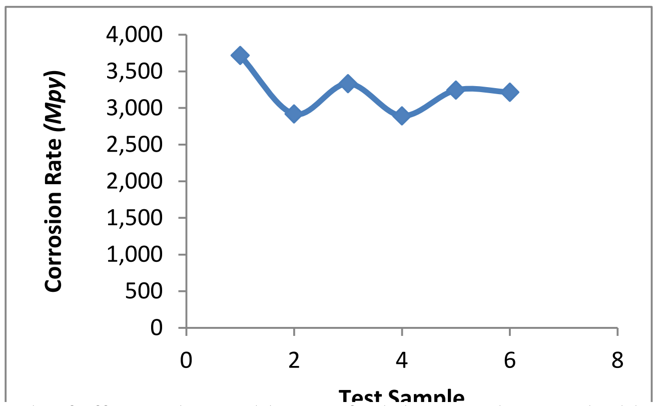

Figure 2. Graph of effect without addition of inhibitor (Paku1) and addition of inhibitor (Paku 2-6) of watermelon rind extract on iron spikes in seawater medium

Inhibition efficiency

The administration of extract inhibitors in watermelon on the samples of iron nails used can slow down the corrosion rate of the iron nails either by immersion in a 3% NaCl medium or a seawater medium. The inhibitory efficiency of the extract used depends on the concentration of the inhibitor. Inhibition efficiency tends to increase for each addition of inhibitor concentration. It can be seen in **Figures 3** and **4**.

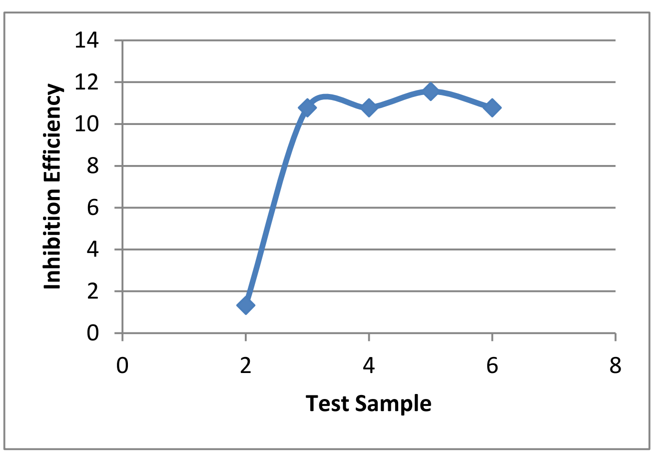

Figure 3. Graph of inhibition efficiency of peel extract in watermelon in 3% NaCl medium

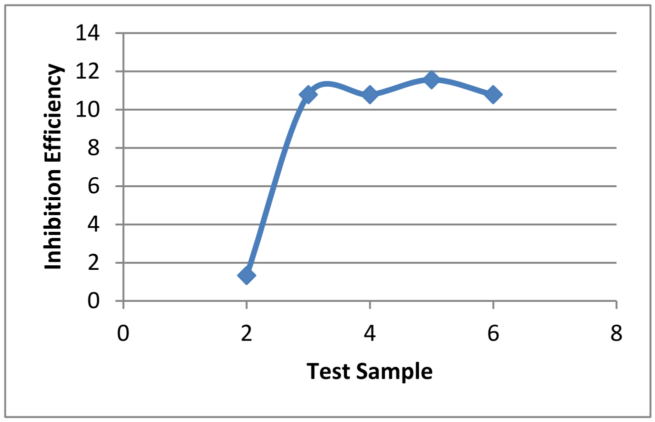

Figure 4. Graph of inhibition efficiency of peel extract in watermelon in seawater medium.

The inhibition efficiency of rind extract in the resulting watermelon varies depending on the concentration of the inhibitor and the corrosive medium. Based on Figure 4, it can be seen that with increasing inhibitor concentration, the inhibition efficiency also increases. Inhibition efficiency in 3% NaCl corrosive media can reach 11.56% at 8% inhibitor concentration, inhibition efficiency in seawater corrosive medium reaches 22.15% inhibitor concentration 4%. The highest inhibitory efficiency produced was at 8% inhibitor concentration for 3% NaCl corrosive medium and 4% inhibitor concentration in seawater medium. This was due to the Fe complex compound being formed entirely and covering the entire steel surface. However, at 2% and 16% inhibitor concentrations, the inhibition efficiency decreased. This is because, at this concentration, the inhibitor can no longer function properly to coat the iron surface so that corrosive ions will attack the nail (Wahyuni & Syamsudin, 2014).

A chemical inhibitor is a chemical substance that can inhibit or slow down a chemical reaction. Working specifically, the corrosion inhibitor is a chemical substance that, when added to a particular environment, will reduce the corrosion rate of metal due to the surrounding environment. Organic inhibitors are derived from organic materials with compounds capable of forming complexes. The inhibitor used in this study was the peel extract in watermelon, which was analyzed to contain citrulline compounds (Dalimunthe, 2004).

Different corrosive mediums produce different corrosion rates. When viewed from the results of the study, iron nails soaked in 3% NaCl had a higher corrosion rate of 886.1859 Mpy compared to iron nails soaked in natural seawater, which was 786.0650 Mpy. that is equal to 15.34% at a concentration of 3% inhibitor with 3% NaCl corrosive media. Meanwhile, a study conducted by (Setia, 2015) using mango leaves as an organic inhibitor resulted in the highest inhibition efficiency of 16.725% at an inhibitor concentration of 300 ppm.

Artificial seawater has a more significant opportunity for corrosion processes in a metal material than natural seawater. This is because there are still Mg^{2+} and Ca^{2+} ions in natural seawater. The presence of ions can reduce the corrosion rate because of their ability to form layers of $CaCO_3$ and $Mg(OH)_2$ on the material's surface, resulting from the cathodic reaction of oxygen on the metal surface (Schumacher, 1999). NaCl solution is an example of artificial seawater that is most often used in research because, in NaCl solution, ions (Na^+ and Cl^-) will be formed which causes this solution to be able to produce a conductivity value to connect the anode and cathode and can also accelerate the corrosion rate that occurs with electrochemical reactions (Arenas et al., 2002).

Conclusions

The addition of rind extract in watermelon can reduce the value of the corrosion rate on iron nails both in a 3% NaCl corrosive medium and in seawater. The highest inhibition efficiency produced 3% NaCl medium lies in the inhibitor with a concentration of 8%, and with seawater, the medium lies in the inhibitor with a concentration of 4%. The inhibition efficiency values were 11.56% and 22.15%, respectively.

Acknowledgment

Thanks are conveyed to the head of the Chemistry laboratory, FKIP Tadulako University.

References

Abdurahman, F. (2010). *Pengaruh waktu perendaman baja karbon rendah dengan penambahan ekstrak ubi ungu sebagai green corrosion inhibitor di lingkungan HCl 1 M*. Jakarta: Universitas Indonesia.

Ahammed, M. (1998). Probabilistic estimation of remaining life of a pipeline in the presence of active corrosion defects. *International Journal of Pressure Vessels and Piping, 75*(4), 321-329.

Arenas, M. A., Conde, A., & Damborenea, J. J. d. (2002). A suitable green corrosion inhibitor for tinplate. *Corrosion Science, 44*(3), 511-520.

Dalimunthe, I. S. (2004). Kimia dari inhibitor korosi. Unpublished Undergraduate's thesis. Medan: Universitas Sumatera Utara.

Dariva, C. G., & Galio, A. F. (2014). Corrosion inhibitors–principles, mechanisms and applications. In M. Aliofkhazraei (Eds.), *Developments In Corrosion Protection* (pp 365-379). London: InTech.

Favre, M., & Landolt, D. (1993). The influence of gallic acid on the reduction of rust on painted steel surfaces. *Corrosion Science, 34*(9), 1481–1494.

Gunaatmaja, A. (2011). *Pengaruh waktu perendaman terhadap laju korosi pada baja karbon rendah dengan penambahan ekstrak ubi ungu sebagai inhibitor organik di lingkungan NaCl 3,5%.* Jakarta: Universitas Indonesia.

Harborne, J. B. (1996). *Metode fitokimia penuntun cara modern menganalisis tumbuhan.* Bandung: Institut Teknologi Bandung.

Hosary, A. A. E., Saleh, R. M., & Din, A. M. S. E. (1972). Corrosion inhibition by naturally occurring substances—I. The effect of hibiscus subdariffa (karkade) extract on the dissolution of Al and Zn. *Corrosiun Science, 12*(12), 897-904.

Ilim, I., Pandiangan, K. D., & Sudrajat, S. (2007). Studi penggunaan tumbuhan tembakau, teh dan kopi sebagai inhibitor korosi baja lunak dalam air laut buatan yang jenuh CO_2. *Jurnal MIPA FMIPA Universitas Lampung, 13*(2), 163–168.

Irianty, R. S., & Khairat. (2013). Ekstrak daun pepaya sebagai inhibitor korosi pada baja AISI 4140 di medium air laut. *Teknobiologi, 4*(2), 77-82.

Nasution, Y. R. A., Hermawan, S., & Hasibuan, R. (2012). Penentuan efisiensi inhibisi reaksi korosi baja menggunakan ekstrak kulit buah manggis (garcinia mangostana l) *Jurnal Teknik Kimia USU, 1*(2), 45-48.

Nurdin, I., & Syahri, M. (1999). Inhibisi korosi baja karbon di dalam larutan karbonat bikarbonat. *Journal of Mathematical and Fundamental Sciences, 31*(1), 19-23.

Odewunmi, N. A., Umoren, S., Gasem, Z. M., Ganiyu, S., & Qamaruddin, M. (2015). L-Citrulline: An active corrosion inhibitor component of watermelon rind extract for mild steel in HCl medium. *Journal of the Taiwan Institute of Chemical Engineers, 51*, 177-185.

Poursaee, A. (2011). Corrosion measurement techniques in steel reinforced concrete. *Journal of ASTM International, 8*(5), 1-15.

Prihandani, S. S., Andriani, S. M. N., & Poeloengan, M. (2016). Efektivitas ekstrak biji mangga harumanis terhadap staphylococcus aureus, bacillus subtilis, shigella sp., dan escherichia coli. *Veteriner, 17*(15), 45-50.

Purnomo, A., & Sumarji, S. (2015). Pengaruh variasi konsentrasi inhibitor ekstrak kulit buah kakao terhadap laju korosi pipa baja karbon A53 pada media air laut. *ROTOR, 8*(1), 19-24.

Sari, D. M., Handani, S., & Yetri, Y. (2013). Pengendalian laju korosi baja St-37 dalam medium asam klorida dan natrium klorida menggunakan inhibitor ekstrak daun teh (camelia sinensis). *Jurnal Fisika Unand, 2*(3), 204-211.

Schumacher, M. (1999). *Seawater corrosion handbook*. New York : Noyes Data Corp.

Setia, D. (2015). *Penghambatan laju korosi dengan memanfaatkan ekstrak daun mangga (mangifera indica l) sebagai inhibitor korosi*. Unpublished diploma's thesis. Palembang: Politeknik Negeri Sriwijaya.

Tandjaja, A. K. (2013). *Peningkatan jumlah sel fibroblas akibat pemberian ekstrak biji semangka (citrullus lanatus) pada penyembuhan luka*. Unpublished Undergraduate's thesis. Surabaya: Universitas Airlangga Surabaya.

Wahyuni, T., & Syamsudin Ab. (2014). Pemanfaatan tanin ekstrak daun jambu biji terhadap laju korosi besi dalam larutan NaCl 3% (w/v). *Konversi, 3*(1). 45-52.

Widyastuti, Y. E., Paimin., & Farry, B. (1993). *Mengenal buah unggul Indonesia*. Jakarta: Penebar Swadaya.

Wu, G., Collins, J. K., Perkins-Veazie, P., Siddiq, M., Dolan, K. D., Kelly, K. A., & Meininger, C. J. (2007). Dietary supplementation with watermelon pomace juice enhances arginine availability and ameliorates the metabolic syndrome in Zucker diabetic fatty rats. *The Journal of Nutrition, 137*(2), 2680-2685.

Zakaria, Z. A., Harmami., & Ulfin, I. (2016). L-citrulline sebagai inhibitor korosi pada tinplate dalam media Nacl. *Jurnal Sains dan Seni ITS, 5*(1), 14-16.