

ZIBELINE INTERNATIONAL
PUBLISHING

ISSN: 2716-7100 (Online)

CODEN: MCEMC2

Materials & Corrosion Engineering Management (MACEM)

DOI: <http://doi.org/10.26480/macem.02.2020.39.42>

CrossMark

RESEARCH ARTICLE

USING ONE OF ORGANIC EXTRACTS AS A CORROSION INHIBITOR FOR CARBON STEEL IN ACIDIC ENVIRONMENT

A. Ngatin*, R.P. Sihombing

Department of Chemical Engineering, Politeknik Negeri Bandung, Bandung, Indonesia.

*Corresponding Author Email: angatin5@yahoo.com

This is an open access article distributed under the Creative Commons Attribution License CC BY 4.0, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

ARTICLE DETAILS

Article History:

Received 15 May 2020

Accepted 20 June 2020

Available online 14 July 2020

ABSTRACT

Utilization of mangosteen rind extract as carbon steel inhibitors in the environment of hydrochloric acid (HCl) 0.1M, 0.5M, and 1.0M. Extracts were carried out by extraction using ethanol solvent at a temperature of 60°C with a time of 80 minutes. The variation of extract concentration (100 ppm to 1000 ppm in 3 days and the effect of time of corroding the carbon steel with the addition of 1000 ppm extract. Corrosion rate is calculated based on the difference in weight and corrosion products shown by microscope optics. The objective was investigated corrosion inhibition efficiency that could be prevented by mangosteen peel extract as inhibitor. The results showed inhibitory properties of mangosteen peel extract for three (3) days increased with increasing extract concentrations up to 76.53% in 0.1M HCl solution and 28.83% in 1.0M HCl solutions. For the addition of 1000 ppm mangosteen peel extract showed inhibitor efficiency reached about 90% at 3 days of corrosive time in HCl 0, 5 M, 87% in 1.0 M HCl solution, and 81% in 0.1 M HCl solution. The experiment showed that the process of diffusion of compounds in extracts on the surface of carbon steel and react with ferro ions (Fe^{2+}) to form chemical covalent coordination coordinate with a thickness of 76 μm was successfully done.

KEYWORDS

hydrochloric acid, carbon steel, microscope optics, mangosteen peel.

1. INTRODUCTION

Mangosteen rind extract produced 6 xanthone derivatives (Shan et al., 2011). Namely alpha mangostin, beta-mangostin, gama-mangostin, mangostinone, garcinone E, and 2-isoprenyl-1,7-dihydroxy-3-methoxyxanton, topophyllin B, mangostanol, flavonoids epicatechin, and gartanin (Ele et al., 2018). Xanthones are kind of organic compound, in phenol compounds that are found in very high concentrations in the skin of mangosteen (*Garcinia mangostana*). Xanthone compounds are antioxidants found in mangosteen peel with high levels and have good and beneficial properties for the body, such as anti-inflammation, anti-diabetes, anti-cancer, anti-bacterial, anti-fungal, anti-plasmodial, and able to increase immunity (Miryanti et al., 2011). Mangosteen rind is brown to purple. Components that contribute to the brown-purple color of mangosteen peel are pigments called anthocyanins such as cyanidin-3-sophoroside and cyanidin-3-glucoside (Kaewsukseng et al., 2019). To extract the compounds contained in the mangosteen rind extraction process is carried out using ethanol (96%) (Ulfah and Karsa, 2007). Solvents can be recycled and their waste or raffinate can be used as plant fertilizer.

Corrosion is the event of damage to metal material due to reacting with the environment, so that it can result in large losses (Garcia-Arriaga et al., 2010). The cost of losses incurred due to corrosion includes maintenance costs, replacement of corroded equipment and components, labor costs, and indirect costs such as costs of production decline due to having to shut

down and decrease service life. Corrosion events on metal materials cannot be stopped at all, but can be controlled and prevented from the start. Failure to control corrosion will have an impact on economic losses and threaten the safety of human life and the environment. The annual direct cost of corrosion for infrastructure is estimated to be US\$300 billion in the US and €200 billion in Europe (Bohm, 2014). It is almost impossible to prevent corrosion, however there are some alternative ways to control it (Brondel et al., 1994; Finsgar and Jackson, 2014). Therefore, it is necessary to control corrosion from the beginning by selecting corrosion resistant materials and design, using adequate coatings and suitable inhibitors and cathodic protection to increase the useful life of equipment and components and reduce the risk of accidents (Knudson and Forsgren, 2017).

Inhibitors are chemicals that with low concentrations added to environmental media will slow the rate of metal corrosion. The use of inhibitors is one for controlling corrosion and is generally used for corrosion prevention on the inside of structures such as pipes, vessels and storage tanks. At present, corrosion control with inhibitors still uses organic and inorganic chemicals. The use of these chemicals will have an impact on environmental pollution. To reduce environmental pollution an attempt is made to use inhibitors from natural ingredients. Mangosteen peel is a natural material that is a waste and in mangosteen peel contains alkaloid compounds and contains compounds that are antioxidants (Xin et al., 2016). These alkaloid compounds and antioxidant properties can be used as corrosion inhibitors.

Quick Response Code



Access this article online

Website:

<https://macej.com.my>

DOI:

10.26480/macem.02.2020.39.42

Alkaloid compounds contained in mangosteen peel are xanthon, tannins, catechin, pectin, rosin, and coloring agents, so that they are often used as anti-rust paint ingredients (Glenn et al., 2013). The tannin content in mangosteen peel extract which may be used to inhibit the rate of corrosion of carbon steel. Previous studies have shown that the use of mangosteen peel extract as a corrosion inhibitor in the 0.1 M NaCl environment can reduce corrosion rates with efficiency reaching 75% efficiency at a concentration of 1000 ppm (Asdim, 2008). So that in this study focused on the mechanism of inhibition of corrosion by inhibitors and how far the efficiency of corrosion inhibition that can be prevented by inhibitors of mangosteen peel extract results in hydrochloric acid environment (0.1M, 0.5M and 1.0M). Based on the field of application of inhibitors quite broad ranging from the steel industry, the fertilizer industry, the oil and gas industry, power plants, then one of the inhibitor products from mangosteen peel extract is cheap, safe, environmentally friendly and easily available. This is an advantage of using natural inhibitors, especially mangosteen peel extract and the production process is relatively inexpensive and easy to obtain.

2. RESEARCH METHODS

Utilization of mangosteen peel extract as a carbon steel corrosion inhibitor was carried out experimentally in a laboratory, using an analytical balance instrument to calculate the weight difference, copper sulphate electrode(CSE) standard electrodes and multi-meters were used to measure the metal potential compared to the standard. The stages of implementation outlined are as follows. The preparation stage is the stage of preparing the equipment and mangosteen peel extracted into extracts that can be utilized. In addition, preparing 2 x 6 cm cut carbon steel for corrosion testing in the HCl environment of 0.1 M, 0.5 M and 1.0 M with and without mangosteen rind extraction.

Corrosion of carbon steel is carried out in distilled water, HCl solution plus mangosteen rind extract with varying concentrations, followed by variations in the time of the metal corroding process. Carbon steel corrosion rate was calculated based on the weight loss method with the equation r (corrosion rate) = $534 w / (At \rho)$ mpy and the inhibitor efficiency was determined by the equation: $Eff = (r_0 - r_i) / r_0 \times 100\%$, with r_0 : the rate of corrosion of steel in a salt solution without inhibitors and r_i : the rate of corrosion of steel in a salt solution with mangosteen rind extract added (Asdim, 2008). Carbon steel corrosion test results in each environment were sampled to analyze the surface structure of carbon steel, after the process of corrosive with and without inhibitors, a cross section to see the process of inhibition with optical microscope.

3. RESULTS AND DISCUSSION

3.1 Effect of time on carbon steel corrosion in acid solutions

The corrosion time of carbon steel in distilled water and acid solution influences the corrosion rate of carbon steel. The relationship between the corrosion time of carbon steel and the corrosion rate of carbon steel in acidic solutions is shown in figure 1.

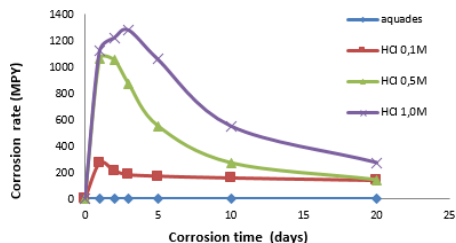
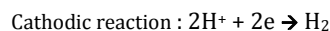
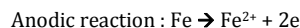


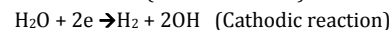
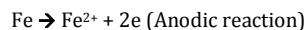
Figure 1: Effect of corrosion time on corrosion rate.

The results of figure 1 show that the longer corrosion time produces more carbon steel corrosion rate, at the beginning it increases until the second day and then the carbon steel corrosion rate decreases. This is due to the rapid corrosion of carbon steel in the beginning which then decreased. At the beginning of the reaction shows the presence of gas bubbles on the

surface of carbon steel that is so fast and after 10 days of corroding the brown solution. This is due to involving carbon steel corrosion reactions in acidic solutions for up to 2 days



The number of hydrogen ions (H^+) at 0.1 M HCl concentration ($\text{pH} = 1$) is much higher than H_2O molecules and the reduction potential of H^+ to hydrogen gas (H_2) is 0.00 volts more positive than the reduction potential of H_2O to hydroxy ions (OH^-) is -0.83 volts Knudsen shows that the formation of hydrogen gas (H_2) is much higher than the formation of OH^- ions negative (-) so that the surface of the carbon steel is quickly corroded (Knudson and Forsgren, 2017). For corrosive times of more than 2 days involves the reaction below.



The reaction of carbon steel in hydrochloric acid solution is faster at increasing concentrations of hydrochloric acid due to the increasing number of H^+ ions in solution and causing carbon steel metal to change its surface faster and even turn black due to oxidation process. Corrosion products are formed due to the reaction of Fe^{2+} with OH^- producing ferro hydroxide [$\text{Fe}(\text{OH})_2$] which in the presence of dissolved oxygen eventually becomes ferric hydroxide [$\text{Fe}(\text{OH})_3$] or forms brown Fe_3O_4 (Jones, 1992).

3.2 Effect of mangosteen peel extract on carbon steel corrosion rate

Mangosteen peel extract affects the rate of corrosion of carbon steel in hydrochloric acid solution as shown in figure 2.

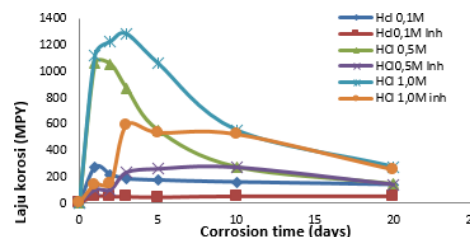


Figure 2: Effect of corrosion time on corrosion rate.

Based on figure 2 it is shown that the corrosion rate of carbon steel in HCl solution without mangosteen rind extract has a higher corrosion rate than the corrosion rate of carbon steel in hydrochloric acid (HCl) solution at the same concentration. This explains that mangosteen peel extract can reduce the corrosion rate of carbon steel in HCl solution. Thus, mangosteen rind extract can be used as a carbon steel corrosion inhibitor in HCl solution, because the inhibitor is a chemical that in low concentrations can reduce the rate of metal corrosion (Gunavathy and Murugavel, 2013). In Figure 2 it is shown that the rate of corrosion of carbon steel rises to the second time of corroding, which then decreases. This is due to carbon steel initially dissolving to produce ferrous ions (Fe^{2+}) on the metal surface, which in turn ferrous ions (Fe^{2+}) binds to chemical compounds contained in the extract through a diffusion process and forms a coordination covalent bond which then coats the metal surface causing the rate carbon steel corrosion decreases (Raja et al., 2016). The effect of mangosteen peel extract concentration on the corrosion rate in 0.1 M, 0.5 M, and 1.0 M HCl solutions is shown in figure 3.

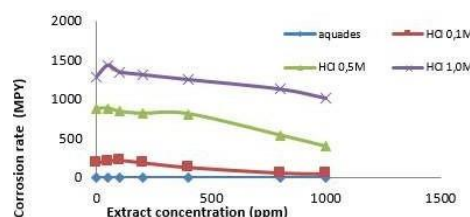


Figure 3: Effect of extract concentration on corrosion rate.

Based on figure 3 it is shown that the corrosion rate of carbon steel in acid solutions is much higher than the corrosion rate of carbon steel in aquades. The higher concentration of mangosteen peel extract results in a lower carbon steel corrosion rate for each concentration of hydrochloric acid (HCl) solution. This shows that mangosteen peel extract able to reduce the corrosion rate of carbon steel in hydrochloric acid solution, so mangosteen peel extract can be used as a corrosion inhibitor. This is due to the mangosteen rind extract containing chemicals or chemical compounds that function as antioxidants (Glenn et al., 2013). Antioxidants are chemicals that lowering oxidation reactions. Oxidation reactions are natural processes that occur in nature and can occur in metals and in the human body. In addition, mangosteen rind extract contains many organic compounds such as tannins, catechin, pectin, rosin which can be used as anti-rust ingredients (Asdim, 2008).

Tannin, pectin, rosin, and xanton compounds are chemical compounds that contain O elements that can be negatively charged and have a pair of free electrons, which are able to bind tightly to the metal through the use of shared electrons on the metal surface, thus coating the metal surface and being able to prevent or hinder the process dissolving metals into solution (Knudson and Forsgren, 2017). This is what causes the carbon steel corrosion rate to decrease (Kumar et al., 2010). Figure 3 also shows that concentration of hydrochloric acid solution affects the rate of corrosion of carbon steels. In this study, the more concentration of hydrochloric acid (HCl), the more corrosion rate of carbon steels is produced. This is due to hydrochloric acid (HCl) is a corrosive solution that is able to corrode carbon steel quickly (Knudson and Forsgren, 2017). The increment of hydrochloric acid (HCl) concentration indicating more corrosivity. Therefore, the corrosion rate also increases since more hydrogen ions (H^+), which is in HCl solution, approaching metal more quickly due to electrons released from the metal dissolving process. Eventually, the carbon steel corrosion process becomes faster.

3.3 Effect of extract concentration on inhibitor efficiency

The concentration of mangosteen rind extract influences the efficiency of its inhibitors as carbon steel corrosion inhibitors in hydrochloric acid solution. The results are shown in figure 4.

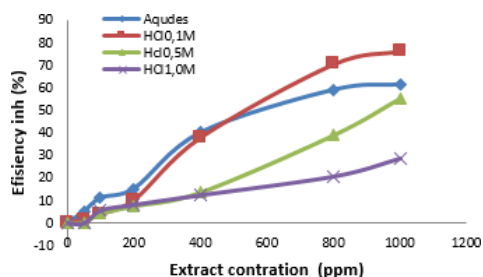


Figure 4: Effect of extract concentration on the efficiency of inhibition.

Figure 4 shows that the concentration of mangosteen peel extract increases the inhibitor efficiency. As shown on the figure 4, in 0.1 M HCl solution reaches 39% for 500 ppm extract concentration and 76.53% for 1000 ppm extract concentration. While for the same extract concentration, the efficiency reach 76.53% in 0.1 M HCl solution and 28.83% in 1.0 M HCl solution. This shows that the more concentrated HCl concentration requires the higher concentration of mangosteen peel extract. Therefore, mangosteen peel extract can be used as a carbon steel corrosion inhibitor in a low concentration of HCl solution more effectively. Based on Asdim's research showed mangosteen peel extract in 0.01 M and 0.02 M HCl acid solution capable of inhibiting carbon steel with inhibition efficiency reaching 77.33% and 75% with a concentration of 1000 ppm for 24 hours (Asdim, 2008).

3.4 The mechanism of performance of mangosteen peel extract as a carbon steel corrosion inhibitor

The mechanism of performance of mangosteen peel extract as a carbon steel corrosion inhibitor in hydrochloric acid (HCl) solution can be

explained that the molecules of chemical compounds contained in mangosteen peel extract move towards the metal surface due to the presence of electrons on the metal surface released by iron metal atoms into ferrous ions (Fe^{2+}) which dissolves in the metal interface (Rani and Basu, 2012). These chemical compounds diffuse and are adsorbed on the metal surface to form chemical bonds with the metal so that it coats the metal surface. The coating caused by a chemical reaction between inhibitor molecules produces a layer that can block the entry of ions contained in the solution, so the metal corrosion process can be inhibited. The reaction between Fe^{2+} ions and natural extract inhibitors produces a chemical bond called a covalent coordination bond, because the inhibitor molecule donates a pair of free electrons to the metal ion.

A pair of free electrons can be found at N, O, or S atoms bound to alkyl or aryl groups (Raja et al., 2016). Molecular chemical compounds contained in mangosteen peel extract contain many hydroxy groups (OH), benzene, methoxy (OCH_3), carbonyl ($C=O$) both in tannin and xanthone compounds which can be diffused and adsorbed on the metal surface, so that the metal surface is coated by the formation of the reaction between chemical compounds contained in mangosteen peel extract with Fe^{2+} ions (Ulfa and Karsa, 2007; Knudson and Forsgren, 2017). Based on experimental data, it was shown visually the layers formed on the metal surface due to the adsorption process of chemical compounds contained in mangosteen peel extract, as shown in figure 5.

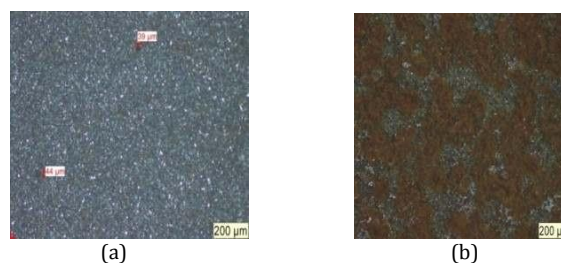


Figure 5: Microphotos of metal surfaces a) without extracts b) with the addition of extracts (5x).

Based on figure 5 it is shown that the metal surface which is corroded in HCl solution without adding mangosteen kulkit extract looks cleaner and black due to the oxidation process (Figure 5a) and there are brown spots with sizes including 44 μm and 39 μm , while the metal surfaces are corroded in HCl solution with mangosteen peel extract contained layers (figure 5b). The coating on the metal surface prevents contact between aggressive ions in solution which can cause corrosion to the metal, so the ions cannot reach the metal surface and the metal is protected from corrosion. The layer on the metal surface is very thin and the thickness of the layer as shown from a cross-section micro photo with a magnification of 20x (a) and 50x (b) in figure 6.

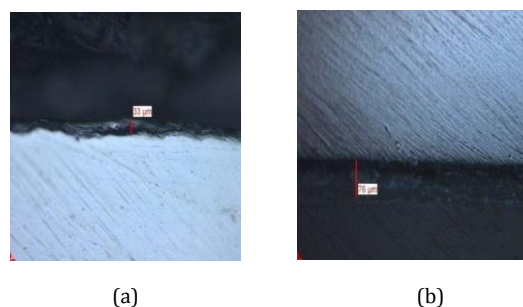


Figure 6: Results of a cross-section micro photo.

Based on figure 6 it is shown that the thickness of the carbon steel surface layer is around 33 μm with a magnification of 20 x (Figure 9a) and about 76 μm at a magnification of 50x (figure 6b).

4. CONCLUSIONS AND SUGGESTIONS

Based on the data and discussion of research results, conclusions can be made including the following. Testing mangosteen peel extract as carbon steel corrosion inhibitor in hydrochloric acid solution for 1000 ppm

extract was able to remove carbon steel for two (2) days with 90% efficiency in 0.5M HCl concentration and 87% in 1.0M HCl with the addition of efficiency getting lower. The mechanism of performance of mangosteen peel extract as a corrosion inhibitor is to coat the metal surface by diffusion and adsorption on the metal surface to form covalently coordinated chemical bonds with a surface layer thickness of around 76 μm .

REFERENCES

- Asdim, A., 2008. Penghambatan Reaksi Korosi Baja Dengan Menggunakan Ekstrak Kulit Buah Manggis (*Garcinia Mangostana L*) Sebagai Inhibitor Dalam Larutan Garam GRADIEN: Jurnal Ilmiah MIPA, 4 (1), Pp. 304-307.
- Böhm, S., 2014. Graphene against corrosion. *Nat Nanotechnol.*, 9 (10), Pp. 741-742.
- Brondel, D., Edwards, R., Hayman, A., Hill, D., Mehta, S., Semerad, T., 1994. Corrosion in the oil industry *Oilfield review*, 6 (2), Pp. 4-18.
- Ele, J.J.G., Migalbin, J.R., Sepelagio, E.G., Jimenez, V.B., Lacia, P.G.F., 2018. Immune Response of Broiler Chickens Fed Diets with Different Levels of Mangosteen (*Garcinia mangostana Linn.*) Rind Powder *Asia Pacific Journal of Multidisciplinary Research*, 6 (2).
- Finšgar, M., Jackson, J., 2014. Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: a review. *Corrosion science*, 86, Pp. 17-41.
- Garcia-Arriaga, V., Alvarez-Ramirez, J., Amaya, M., Sosa, E., 2010. H₂S and O₂ influence on the corrosion of carbon steel immersed in a solution containing 3M diethanolamine. *Corros Sci.*, 52 (7), Pp. 2268-2279.
- Glenn, R.W., Heinrich, J.M., Kaufman, K.M., Hutchins, V.T.H., Dubois, Z.G., Li, J.J., Labitzke, K.M., 2013. U.S. Patent No. 8,349,786 Washington, DC: U.S. Patent and Trademark Office.
- Gunavathy, N., Murugavel, S.C., 2013. Studies on corrosion inhibition of *Musa acuminata* flower extract on mild steel in acid medium. *Asian J. Chem.*, 25 (5), Pp. 2483-2490.
- Jones, J., 1992. *Amino acid and peptide synthesis* Vol. 7 Oxford University Press.
- Kaewsuksaeng, S., Tatmala, N., Shigyo, M., Tanaka, S., Yamauchi, N., 2019. Application of electrostatic atomized water particle suppresses calyx discoloration in relation to postharvest quality of mangosteen (*Garcinia mangostana L.*) *Scientia horticulturae*, 250, Pp.380-387.
- Knudsen, O.Ø., Forsgren, A., 2017. *Corrosion control through organic coatings* CRC Press.
- Kumar, K.P., Pillai, M.S., Thusnavis, G.R., 2010. Pericarp of the fruit of *Garcinia mangostana* as corrosion inhibitor for mild steel in hydrochloric acid medium *Portugaliae. Electrochimica Acta*, 28 (6), Pp. 373-383.
- Miryanti, Y.A., Sapei, L., Budiono, K., Indra, S., 2011. Ekstraksi antioksidan dari kulit buah manggis (*Garcinia mangostana L.*) *Research Report-Engineering Science*, 2.
- Raja, P.B., Ismail, M., Ghoreishiamiri, S., Mirza, J., Ismail, M.C., Kakooei, S., Rahim, A.A., 2016. Reviews on corrosion inhibitors: a short view. *Chemical Engineering Communications*, 203 (9), Pp. 1145-1156.
- Rani, B.E., Basu, B.B.J., 2012. Green inhibitors for corrosion protection of metals and alloys: an overview *International Journal of corrosion*.
- Shan, T., Ma, Q., Guo, K., Liu, J., Li, W., Wang, F., Wu, E., 2011. Xanthones from mangosteen extracts as natural chemopreventive agents: potential anticancer drugs. *Current molecular medicine*, 11 (8), Pp. 666-677.
- Ulfah, D., Karsa, A.L., 2007. Pengaruh tempat tumbuh dan lama penyulingan rendemen minyak atsiri rambu atap (*Baekkea frutescens*) dengan penyulingan metode perebusan *Jurnal Hutan Tropis Borneo*, 8, Pp. 84-88.
- Xin, L.K., Shameli, K., Miyake, M., Kuwano, N., Bt Ahmad Khairudin, N.B., Bt Mohamad, S.E., 2016. Green Synthesis of Gold Nanoparticles Using Aqueous Extract of *Garcinia mangostana* Fruit Peels. *J. Nanomater.*

