RJC

RASĀYAN *J. Chem.*
Vol. 16 | No. 3 |1706-1712| July - September | 2023
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

EFFECTIVENESS OF CACAO FRUIT PEEL EXTRACT *(Theobroma Cacao L.)* AS AN ORGANIC INHIBITOR ON CORROSION OF IRON NAILS IN 3% NaCl MEDIUM

T. Santoso[1,✉], M. R. Jura[1], S. Rahmawati[1], Supriadi[1], S. Y. H. Dapili[1] and Nadrun[2]

[1]Chemistry Education, Faculty of Teacher Training and Education, Universitas Tadulako, Jl. Soekarno Hatta Km 9 Palu, Indonesia, 94118.

[2]English Language Education, Faculty of Teacher Training and Education, Universitas Tadulako, Jl. Soekarno Hatta Km 9 Palu Indonesia, 94118.

✉Corresponding Author: trisantosopalu@gmail.com

ABSTRACT

A Cocoa pod shell is waste that can be used as an organic inhibitor. Cocoa pod skin contains tannins which are raw materials in the manufacture of organic inhibitors. The reason for this research is to ascertain whether cocoa pod extract can influence the rate at which iron nails corrode in a medium containing a 3% NaCl solution. The concentrations of cocoa pod extract utilized were 1%, 2%, 4%, 8%, 16%, and 32%. The results showed that a 3% NaCl medium had the best corrosion rate, namely at a concentration of 16% with a corrosion rate of $0.7038 x 10^{-6}$ g/cm^2.hour and an inhibition efficiency of 81%. In contrast, the corrosion rate in saltwater is 0.8504×10^{-6} g/cm^2 hour and the inhibition efficiency is 63% at a concentration of 4%. According to the study's findings, cocoa shell extract was found to be more efficient against nail erosion at a higher concentration.

Keywords: Cocoa Fruit Peel, Organic Inhibitor, Corrosive Medium, Corrosion Rate, Inhibition Efficiency.

RASĀYAN *J. Chem.*, Vol. 16, No. 3, 2023

INTRODUCTION

Because the corrosion process on metal cannot be avoided or stopped, it is a problem that will always exist. However, its pace can be controlled or slowed in order to cut losses and stop adverse corrosion-related impacts, such as through the application of the coating to metal surfaces. adding corrosion inhibitors, cathodic protection, and other methods. Based on these many techniques, using inhibitors is a successful strategy to prevent corrosion because the price is reasonable and the procedure is straightforward.[1] In this study, inhibitors from organic compounds were used because they are easily degraded so they do not pollute the environment. Organic inhibitors derived from plant parts containing tannins are chemical substances containing N, O, P, and S atoms and atoms that have lone pairs of electrons which can function as ligands that will form complex compounds with metals. Tannins are usually found in the leaves, roots, skin, fruits, and stems of plants.[2] One of them is from the skin of cocoa pods (*Theobroma cacao*) which contains tannins and catechins which are polyphenolic organic compounds belonging to the flavonoid group which can form insoluble complexes with metal ions, so they can be used as corrosion inhibitors on nails.[3] The high tannin concentration of cocoa pods makes it possible to use it to reduce the rate of nail corrosion. In addition, cocoa pod skin is often thrown away and cannot be used optimally. In addition, the price is much cheaper than synthetic inhibitors such as pure tannins.[4] Tannin compounds in cocoa shell extract can form complex compounds with Fe(III) on the metal surface so that the corrosion reaction rate will decrease. This complex compound will block the attack of corrosive ions on metal surfaces.[5] Many studies have been carried out on organic compound inhibitors, including the use of mangosteen rind using NaCl medium with the potentiodynamic method succeeded in reducing corrosion on St-37 steel. The greatest efficiency of corrosion inhibitors occurs at a concentration of 2% mangosteen fruit extract with an efficiency of 26.05%, due to the presence of polyphenols in the form of tannins which can inhibit the corrosion rate.[6] Another organic inhibitor that has been studied is cocoa leaf extract with varying inhibitor concentrations of 1-10%, using the weight loss method with corrosive medium H_2SO_4 3% and Na_2SO_4 3%. The results showed that the extract was also efficient in controlling the corrosion rate due to the presence of tannins.[7] Tambun, *et*

http://doi.org/10.31788/RJC.2023.1638398

al.[8] previously also applied jengkol bark (Pithecellobium jiringa) as a corrosion inhibitor for iron in 3% hydrochloric acid media. Controlling the corrosion rate of steel using organic inhibitors of tea leaf extract has also been carried out by Zakaria, *et al.*[9] with 3% HCl medium and potentiodynamic methods. The results showed that the greater the concentration of inhibitor added, the value of the corrosion rate will decrease and the value of inhibition efficiency will increase. The greatest efficiency value was obtained by adding 10% inhibitor concentration to HCl corrosive medium, which reached 92%. Based on these studies, it can be seen that inhibitor extracts of tea leaves, cocoa leaves, mangosteen, jengkol bark, tobacco, tea, and coffee are very efficient in controlling the corrosion rate in a corrosive medium, due to the presence of tannin compounds in these extracts. Therefore, this study intended to use other organic inhibitors which also contain tannins and in abundant quantities, namely cocoa pod shell waste.

EXPERIMENTAL

Tools and Materials

An analytical balance, a blender, a 40-mesh sieve, a desiccator, a measuring cup, a watch glass, a measuring pipette, a beaker, an Erlenmeyer, an oven, label paper, a spatula, an evaporator, a tube clamp, a filter funnel, test tube, and stirring rod were the instruments utilized in this study. Cocoa pod shells, 10 cm iron nails, filter paper, sandpaper, rust-cleaning solution, 70% ethanol, 1% $FeCl_3$, distilled water, seawater, aluminum foil, and tissues were the materials used in this investigation.

Making Cocoa Fruit Peel Powder

Cleanse 1 kg of fresh cocoa pod skin, cut it into little pieces, and let it dry for 5 days in the open air to eliminate the moisture. The dried cocoa pod skin is blended until it becomes smooth and sifted to obtain cocoa pod skin powder.[10]

Extraction Process

As much as 100 grams of cocoa pod powder is put into an Erlenmeyer and macerated with 600 mL of 70% ethanol, 70% ethanol is used because it can attract both polar and non-polar compounds such as alkaloids, tannins, and flavonoids. After being mixed, the mixture is placed in the macerator for 72 hours. Following that, the filter paper was used to filter the maceration results, and the filtrate was then placed into a rotary vacuum evaporator at 50°C for 10 minutes to create a concentrated extract. The extract results were put into a brown bottle and a qualitative analysis was carried out for the presence of tannins. Results from 6 different concentrations of the concentrated extract—1%, 2%, 4%, 8%, 16%, and 32%—were obtained.[11]

Analyses of Tannin Compounds in Qualitative Form

A beaker containing 10 mL of cocoa pod extract and 10 mL of distilled water was brought to boiling. The filtrate was then collected once it had been filtered. The filtrate was then added to ten drops of 1% $FeCl_3$, and if it turned blue or greenish blue, tannins were present.[12] $FeCl_3$ is used to test samples for antioxidants, which are visible as dark green after adding $FeCl_3$. If the sample contains antioxidants, the dark green hue indicates a positive tannin result.[13]

Preparing Test Samples

Fourteen nail samples are typically sized 10 cm, with a diameter of 0.4 cm, and a weight of 10.5 grams, with 6 samples each treated with different inhibitors and 1 fruit left untreated for immersion in either seawater or NaCl 3%. After using sandpaper to smooth up the nail's surface, it was submerged in 0.1 M sodium carbonate solution for 30 minutes. The nails were then cured for 20 minutes in an oven set to 60°C. After cooling in a desiccator for ten minutes, the initial mass was weighed (W_0).[14]

Making 3% NaCl Solution

Solid NaCl was weighed as much as 3 grams, then added with distilled water to a volume of 100 mL. After that, it was shaken until homogeneous so that a 3% NaCl solution was obtained.

Nail Immersion in Corrosive Media

Nail samples were soaked in two different ways: immersion with no inhibitor solutions added, and without immersion in inhibitor solutions. The employed inhibitor solution's concentrations varied by 1%, 2%, 4%, 8%, 16%, and 32%. While employing 3% NaCl (made seawater) and natural seawater as the test environment or corrosive media to compare corrosion rates.[15]

Determination of Corrosion Rate

The corrosion rate is the rate at which corrosion forms on a metal which is expressed in units of g/cm^2.time (mass per unit area per unit time). The approach to losing weight based on the difference between the starting mass before corrosion testing and the final mass after corrosion testing using equation 1 can be used to measure the efficiency of cocoa pod extract inhibitors to control iron nail sample corrosion rate.[16]

$$Cr = \frac{w_0 - w_1}{\mathrm{A} \times \mathrm{t}} \qquad (1)$$

Information

Cr	Corrosion rate, gram/cm^2.jam.
W_0	Initial mass, grams.
W_1	Final mass, grams.
A	Area of the specimen's surface, cm^2.
t	Elapsed time, hours.

To find the surface area of a nail, the following equation 2 is used:

$$\text{Surface area} = 2\pi r \text{ x } (r + t) \qquad (2)$$

Information

π	Radians; 3.14
r	Radius, cm.
t	Nail height, cm.
2	Constant

Corrosion Inhibition Efficiency

The ability of an inhibitor to slow down the corrosion process on metals is quantified in % units as the effectiveness of corrosion inhibition. The efficiency of corrosion inhibition can be determined using the Tafel extrapolation method in equation 3 as follows:[16]

$$IE = \frac{Cr_0 - Cr_{inh}}{Cr_0} \; x\; 100\% \qquad (3)$$

Information:

IE	Effectivity of Inhibition
Cr_0	Rate of corrosion absent an inhibitor
Cr_{inh}	Rate of corrosion with an inhibitor

RESULTS AND DISCUSSION

Corrosion is a redox reaction with the environment that results in the destruction, erosion, shrinkage, or deterioration of the quality of metal.[17] Tests were carried out on iron nails using two corrosive media, namely 3% NaCl (artificial seawater) and natural seawater as a comparison. This investigates the variation in iron nail corrosion rates in the two corrosive media. The weight loss method, which assesses the weight loss in the test sample as a result of the ongoing corrosion process, is used to quantify the corrosion rate.

Cocoa Fruit Peel Extraction

Extraction is the process of separating, withdrawing, or removing a component of a mixture from the mixture. Usually using a solvent according to the desired component, the liquid is separated and evaporated to a certain concentration.[17] Using the maceration process and 70% ethanol as the solvent, cocoa pod skin was extracted, yielding a 100% concentrated extract. The cocoa pod extract obtained was used as a corrosion inhibitor. The ethanol solvent is a universal solvent that is able to bind all chemical components found in natural plant materials, both semi-polar, non-polar, and polar. Ethanol is a filtered liquid that easily enters the cells through the cell walls of the material so that the secondary metabolites contained in natural products will dissolve in the solvent and the compounds will be extracted perfectly.[18]

Qualitative Investigation of Tannin

The objective of the analysis qualitatively used in this research is to identify the existence of tannin compounds in cocoa shell extract that can slow the rate of iron corrosion. Tannin testing using iron (III) chloride reagent. In order to ascertain whether the sample included phenol groups, which are seen in dark green, 10 drops of $FeCl_3$ were added to a concentrated extract of cocoa shells that had been cooked with 10 mL of distilled water. The sample may contain phenolic compounds, and it's conceivable that one of them is tannin because of the sample's dark green color (Fig.-1). due to the polyphenolic nature of tannins. According to Hamzah *et al.*[13] (2020), adding extracts to a 1% $FeCl_3$ solution in water produced green, red, purple, blue, and dark black hues, which were the traditional colors used to identify simple phenolic compounds.

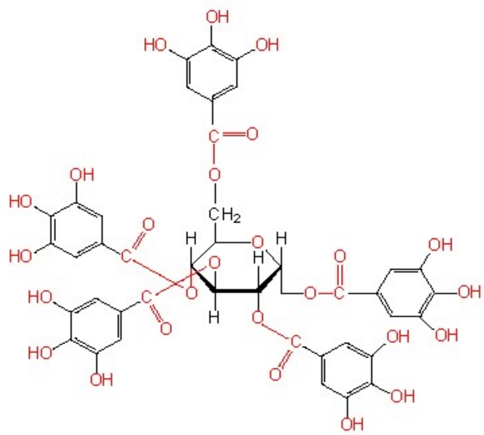

Fig.-1: Structure of Tannin Compounds

Rate of Nail Corrosion

The amount of metal released on the iron surface per unit of time is known as the corrosion rate. In this study, the corrosion rate is measured in grams per square centimeter each hour. During the testing of the corrosion rate of iron nails in 3% NaCl medium and seawater with a soaking time of 168 hours, it was found that there was a difference between the iron nail samples added with inhibitor solution and those without added inhibitor solution of cocoa pod extract in both 3% and 3% NaCl solution medium in seawater. Tables-1 and 2 show this distinction.

Table-1: Iron Nail Corrosion Rates in 3% NaCl Medium

No.	Sample	Corrosion rate (g/cm^2.hour)
1	Nail 1 (control/without the addition of inhibitors)	3.7211×10^{-6}
2	Nail 2 (addition of inhibitors 1%)	1.6657×10^{-6}
3	Nail 3 (addition of inhibitors 2%)	1.7525×10^{-6}
4	Nail 4 (addition of inhibitors 4%)	1.3009×10^{-6}
5	Nail 5 (addition of inhibitors 8%)	0.9567×10^{-6}
6	Nail 6 (addition of inhibitors 16%)	0.7038×10^{-6}
7	Nail 7 (addition of inhibitors 32%)	1.9859×10^{-6}

According to a study, 3% NaCl solution media and seawater media can both modify how rapidly iron nails corrode by adding cocoa pod extract. This is because cocoa pod extract contains tannic components. As illustrated in Fig.-2, the tannin components in cocoa pod extract can combine with Fe (III) to produce complex compounds on metal surfaces.[3]

Because of the inclusion of inhibitors at concentrations of 1%, 4%, 8%, and 16%, the rate of corrosion reaction in a 3% NaCl medium was reduced. Because the Fe (III) complex molecule will stop corrosive ions from attacking the metal surface, the rate of the corrosion reaction will be slowed down. When the inhibitor was added at a concentration of 32%, the corrosion rate also increased. In contrast, in a seawater

RASĀYAN *J. Chem.*
Vol. 16 | No. 3 |1706-1712| July - September | 2023

medium, the corrosion rate rose at concentrations of 8-32% when inhibitors were added at 1%, 2%, and 4% concentrations. This is because the Fe-tannin extract layer can't completely cover the nail's surface, allowing the unprotected area to ionize and corrode. Also, the tannin extract contains contaminants that adhere to the nail surface and impair the quick corrosion rate.[19]

Table-2: Corrosion Rate Values of Iron Nails in Seawater Medium

No.	Sample	Corrosion rate (g/cm^2.hour)
1	Nail 1 (control/without the addition of inhibitors)	2.3468×10^{-6}
2	Nail 2 (addition of inhibitors 1%)	1.5201×10^{-6}
3	Nail 3 (addition of inhibitors 2%)	1.327×10^{-6}
4	Nail 4 (addition of inhibitors 4%)	0.8504×10^{-6}
5	Nail 5 (addition of inhibitors 8%)	1.2903×10^{-6}
6	Nail 6 (addition of inhibitors 16%)	0.9107×10^{-6}
7	Nail 7 (addition of inhibitors 32%)	1.4928×10^{-6}

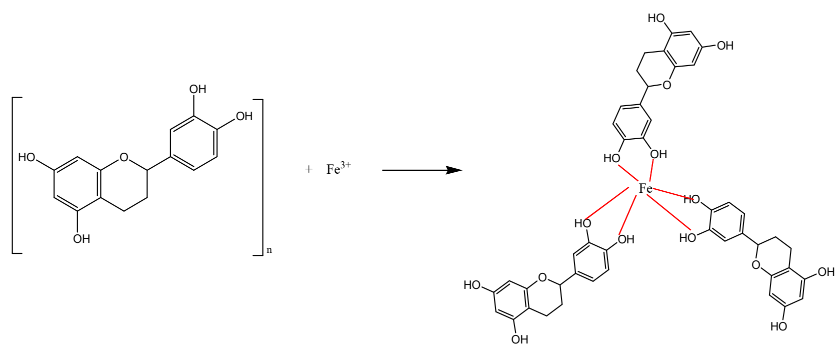

Fig.-2: Tannin Complex Structure with Fe(III)

Inhibition Efficiency of Cocoa Fruit Peel Extract

A thin coating of inhibitors the thickness of several inhibitor molecules will first form on the metal surface after being applied to a test sample. Although it cannot be seen with the human eye, this coating can prevent environmental attacks on the metal. Furthermore, environmental influences, it will cause the inhibitor to precipitate and protect the iron surface against corrosion.[20] The inhibition efficiency of organic compounds depends on their adsorption properties. The presence of electrons and heteroatoms greatly influences the nature of this adsorption, this enhances the inhibitor molecules' ability to bind to the metal surface.[21] Administering cocoa pod extract inhibitors can change how quickly iron nails corrode, whether they're submerged in seawater or a solution with 3% NaCl. Tables-3 and 4 demonstrate this.

Table-3: Value of Inhibition Efficiency of Iron Nails in 3% NaCl Medium

No.	Sample	Inhibition Efficiency
1	Nail 2 (addition of inhibitors 1%)	55%
2	Nail 3 (addition of inhibitors 2%)	52%
3	Nail 4 (addition of inhibitors 4%)	65%
4	Nail 5 (addition of inhibitors 8%)	74%
5	Nail 6 (addition of inhibitors 16%)	81%
6	Nail 7 (addition of inhibitors 32%)	46%

Sending out inhibitors can make inhibition more valuable by reducing the rate of corrosion. Its effectiveness serves as a gauge of its ability to suppress. The effectiveness value is dependent on the inhibitor's concentration. How effectively the resulting cocoa shell extract suppresses the process depends on the concentration of the inhibitor and the corrosive medium. Tables-3 and 4 show that as inhibitor concentration rises, the effectiveness of the inhibition likewise rises. At a 16% inhibitor concentration, inhibition efficiency in 3% NaCl corrosive medium can reach 81%, but only 63% at a 4% inhibitor concentration in

Vol. 16 | No. 3 |1706-1712| July - September | 2023

seawater corrosive media. The best efficiency is thus achieved at a concentration of 16% for a medium containing a 3% NaCl solution and a 4% concentration for a medium containing seawater. This is due to the fact that under these circumstances, the Fe-tannin complex does not fully form and totally covers the nail surface (Fig.-2).

Table-4: Value of Inhibition Efficiency of Iron Nails in Seawater Medium

No.	Sample	Inhibition Efficiency
1	Nail 2 (addition of inhibitors 1%)	35%
2	Nail 3 (addition of inhibitors 2%)	43%
3	Nail 4 (addition of inhibitors 4%)	63%
4	Nail 5 (addition of inhibitors 8%)	45%
5	Nail 6 (addition of inhibitors 16%)	61%
6	Nail 7 (addition of inhibitors 32%)	36%

However, the effectiveness of inhibition was reduced at a concentration of 32%. This is due to the inhibitor's decreased ability to perfectly coat the nail surface at this concentration; in other words, it is unable to create Fe-tannin at this concentration, which causes corrosive ions to damage the nail. Different corrosion rates and inhibition efficiencies are caused by differences in the corrosive medium being employed. According to the study's findings, iron nails soaking in saltwater had a corrosion rate value of 2.3468×10^{-6} g/cm^2 hour while the iron nails soaking in 3% NaCl had a value of 3.7211×10^{-6} g/cm^2 hour. With a 3% NaCl corrosive medium and a 16% inhibitor concentration, 81% inhibition efficiency was the highest. Compared to natural seawater, artificial seawater (NaCl 3%) has a higher likelihood of causing corrosion in a metal material. This occurs because Mg^{2+} and Ca^{2+} ions are still present in natural seawater. Due to their capacity to create layers of $CaCO_3$ and $Mg(OH)_2$ on the surface of the material as a result of cathodic oxygen on the metal surface, These ions can slow down corrosion when they are present.[22]

CONCLUSION

Iron nails' corrosion rates in both saltwater and a 3% NaCl corrosive solution can change when cocoa pod extract is added. Based on the test results, the best corrosion rate in 3% NaCl medium is at a concentration of 16% with a corrosion rate of 0.7038×10^{-6} g/cm^2 hour and an inhibition efficiency of 81%. Whereas in seawater medium, that is at a concentration of 4% with a corrosion rate of 0.8504×10^{-6} g/cm^2 hour and an inhibition efficiency of 63%. According to the study's findings, cocoa shell extract was found to be more efficient against nail damage at larger concentrations.

ACKNOWLEDGEMENTS

Thanks to the Faculty of Education, Tadulako University for the year 2023 funding for this research.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

T. Santoso http://orcid.org/0000-0003-0959-3626
M.R.Jura http://orchid.org/ 0009-0003-3564-1940
S. Rahmawati http://orchid.org/ 0000-0002-7954-4822
Supriadi http://orchid.org/ 0000-0001-6432-4109
S. Y. H. Dapili http://orchid.org/ 0009-0004-6598-8563
Nadrun http://orchid.org/ 0009-0004-3509-741X

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[RJC-8398/2023]