Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.7 No.4, 2015

Utilization of Natural Tannin Extract for Copper Corrosion Inhibitor in Hydrochloric Acid Solution

Resa Denasta Syarif* Suprihatin Prayoga Suryadarma
Department of Agroindustrial Technology, Faculty of Agricultural Engineering and Technology,
Bogor Agricultural University, IPB Darmaga Campus, 16002, Indonesia
Email : resadenasta@yahoo.com

Abstract
Inhibitor of copper corrosion in 1M hydrochloric acid (HCl) solution by utilizing natural tannin extracted from raw gambier (*Uncaria gambier* Roxb.), areca nut (*Areca catechu*) and mangosteen peel (*Garcinia mangostana*) was investigated. Tannin functional groups were detected by FTIR analysis, the effect of tannin source and tannin concentration in copper corrosion inhibition were investigated by weight loss method (gravimetric). The ability of the best inhibitors was derived from raw gambier-based solution with lowest corrosion rate of 37.06 mils per year (mpy), followed by areca nut 45.34 mpy and mangosteen peel 49.49 mpy. The best concentraction of inhibitor was 0.75% which gives highest activation energy value and good surface appearance of the copper plate.
Keywords: copper, corrosion rate, corrosion inhibitor, raw gambier, areca nut, mangosteen peel

1. Introduction

Copper is a metal which is widely used in industry and domestic, for heating and cooling systems, machining, as a conductor of the power source and the drain pipe material for water (including sea water). Based on data from the Copper Development Association (2014), the use of copper in the world, among others, as a construction material (51%), non-electrical equipment material (15%), transportation material (13%), electrical equipment material (13%) and others (8%).

Although it has many advantages, copper faces problem relating with corrosion. The impacts of corrosion are very dangerous. It can cause equipment damage, explosion, fire, and environmental pollution which can cause human death and high material loss. World's handling costs due to corrosion per year reaches $ 1.8 trillion (Schmitt, 2009). The occurance of corrosion can not be totally stoped but the rate of corrosion can be inhibited.

Addition of inhibitor is a method to overcome corrosion problem but the use of non-organic inhibitor no lo longer good when aplicated to equipment that related to food production. The solution of this problem is by using organic inhibitor material which not only save for food production but also enviromental friendly and has abundant availability. An organic material which has potential to be developed as corrosion inhibitor is tannin.

Tannin is water-soluble phenolic compounds, having molecular weights between 500 and 3000. It giving the usual phenolic reactions and having special properties such as the ability to precipitate alkaloids, gelatine and other proteins. it also has antioxidative properties. There are some researches related to corrosion inhibition which used tannin as corrosion inhibitor materials. Tannin from tea (*Camellia sinensis*) (Loto, 2011), mimosa (*Acacia mearnsii* DeWild.) bark (Peres, 2013) and oil palm empty fruit bunch (Ibrahim *et al.*, 2005) were utilized as material for corrosion inhibitor in mild steel, whereas, mangrove (*Rhizopora apiculata*) bark was utilized as corrosion inhibitor material for copper (Shah *et al.*, 2010).

Based on tannin ability to inhibit corrosion, this reseach was observed some material containing tannin which has abundant availability to be utilized as corrosion inhibitor for copper. There are three commodities which have not utilized yet as corrosion inhibitor in copper, they are raw gambier, areca nut and mangosteen peel. Gambier has antioxidative activity which indicate that tannin is one of gambier component (Anggraini *et al*., 2011). Areca nut and mangosteen peel also have component which has antioxidative activity (Xing *et al.* 2010, Suttirak and Manurakchinakorn , 2014) that also indicate existance of tannin in those material.

Raw gambier production in Indonesia per year reaches 17,000 tons, whereas areca nut production is 70,000 ton per year (wet basic) and mangosteen peel production is 125,460 tons per year. Three of them have potential contain tannin, thus, in this research the three materials will be used for corrosion inhibitor for copper in extreme medium which is hydrochloride acid (HCl). The main objective of this research is to produce the best inhibitor for copper which enviromental friendly, whereas the spesific objective of this research are to observe the influence of tannin source and to find the effective concentration of inhibitor in corrosion rate inhibitor of copper in HCl 1 M.

2.Methods

2.1 Material and equipment

Materials used were raw gambier, areca nut, mangosteen peel, bioethanol, HCl, Follin Denis reagent, and copper

plate whereas equipments used were glass equipment, disc mill, spectrophotometer, Fourier Transform Infrared (FTIR) ABB MB3000, oven, thermometer, analytical balance, vacuum filter, digital camera and USB microscope 400x zoom

2.2 Experimental Procedure

Raw gambier, areca nut and mangosteen peel was milled by disc mill end extracted by 70° C water solvent. Supernatant from the mixture is part which containing tannin was dried by spray drier. Fourier Transform Infrared (FTIR) analysis was performed with FTIR ABB MB3000. Tannin content measurement was done by using AOAC 952.03 method (2005).

Corrosion rate and inhibitor efficiency was measured by gravimetric method (Zarrouk *et al.*, 2011, Fouda *et al.*, 2011, Shah *et al.*, 2011). The copper specimens of size 10 mm x 10 mm x 0.5 mm for weight loss measurements were polished abrasive paper from 400 up to 1000, washed with distilled water, degreased with acetone and dried before immersing into the test solution. The experiment was carried out in a test tube containing 10 ml test solution. After 24 h of immersion in 1 M hydrochloric acid solution with and without the addition of tannin with different source, the specimen was withdrawn, rinsed with distilled water, washed with acetone, dried and weighed.

The best source tannin will be used to another gravimetric test with tannin concentration of 0.00% (blank), 0.50%, 0.75% and 1.00% for 24 hours at 303 K, 308 K, 313 K and 318 K to obtain activation energy of sytem and the effective concentration of tannin for corrosion inhibition. Corrosion rate, inhibitor efficiency and activation energy were calculated by following equation :

$$CR = \frac{K.(W_0 - W_1)}{D \times A \times T} \quad \text{..... (1) (ASTM, 2004)}$$

$$IE = \frac{CR_0 - CR_1}{CR_0} \times 100\ \% \quad \text{..... (2) (Sherif, 2012)}$$

$$\ln CR = \ln\left(\frac{-Ea}{R.T}\right) + A \quad \text{..... (3) (Obot, 2009)}$$

Where :

CR = corrosion rate (mils per year, mpy)
W_0 = initial copper weight
W_1 = copper weight after immersion in HCl
K = conversion constant to mpy: 3.45×10^6
D = density of copper (8.93 g/cm$^{3)}$
A = surface width (cm^2)
T = immersion time (hour)

IE = inhibitor efficiency (%/)
CR_0 = corrosion rate without inhibitor (mpy)
CR_1 = corrosion rate with inhibitor (mpy)
Ea = activation energy (J/mol)
R = universal gas constant (8.314 J/mol.K)
T = temperature (K)
A = Arhenius constant

3. Result and Discussion

3.1 Tannin Extract Characterization

At first, tannin content in extract solution was analyzed by indicating tannin functional group in the solution. The existance or tannin was indicated by alcohol and fenol functional group (3550-3200 cm^{-1}), aromatic carbon ring (1700-1400 cm^{-1}), and carboxyl functional group (1300-1000 cm^{-1}). The result of FTIR analysis can be seen in Figure 1. Alcohol and fenol functional group in raw gambier was found in wavelength of 1636 cm^{-1}, 1520 cm^{-1}, 1412 cm^{-1} and carboxyl functional group was found in wavelength of 1296 cm^{-1}, 1250 cm^{-1},1203 cm^{-1},1149 cm^{-1}, 1080 cm^{-1}, 1026 cm^{-1}. Alcohol and fenol functional group in areca nut was found in wavelength of 3425 cm^{-1} whereas aromatic carbon was found in wavelength of 1528 cm^{-1} and 1450 cm^{-1}, and carboxyl funtional group was found in wavelength of 1288 cm-1 and 1111 cm-1. Alcohol and fenol functional group in mangosteen peel was found in wavelength of 3425 cm^{-1} whereas aromatic carbon was found in wavelength of 1412 cm^{-1} and carboxyl funtional group was found in wavelength of 1149 cm^{-1}, 1080 cm^{-1} and 1026 cm^{-1}. Thus, all of tannin source has tannin structure and tannin content can be obtained. Highest yield of tannin extraction was obtained by areca nut i.e 0.5494±0.0011%, followed by raw gambier 0.4503±0.0076 and mangosteen peel 0.1883±0.0027%.

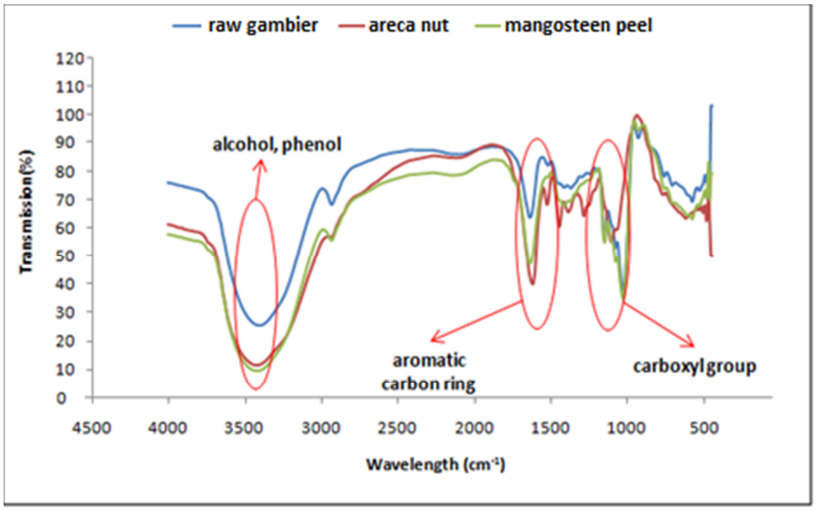


Figure 1. Graph of FTIR Analysis from Different Source Tannin Material

3.2 Influence of Tannin Source to Corrosion Rate

Figure 2 shows the effect of tannin extracted from raw gambier, areca nut and mangosteen peel on copper corrosion rate in the 1 M HCl solution. Raw gambier has the biggest inhibitor efficiency, i.e 80.54%, followed by areca nut 75.19% and mangosteen peel 74.01%. Corrosion rate of copper without addition of inhibitor was 190,46 mpy. The additon of inhibitor significantly decrease the rate of corrosion, which is only 37.06 mpy with the addition of tannin from raw gambier, 45.34 mpy with addition of tannin from areca nut and 49.49 mpy with addition of tannin from mangosteen peel. Therefor, tannin material which was used in determining the best concentration was from raw gambier.

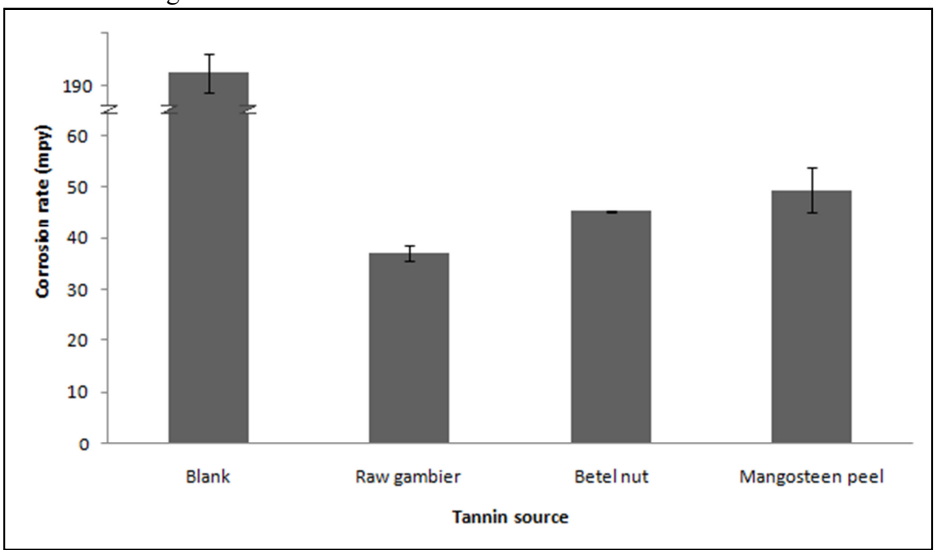


Figure 2. Copper Corrosion Rate in 1M HCl with and without Addition of Tannin from Different Source in 24 Hours at Room Temperature

3.3. *Influence of Tannin Concentration to Corrosion Rate*

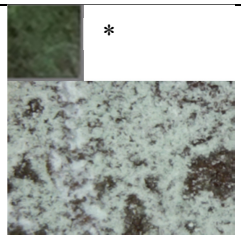
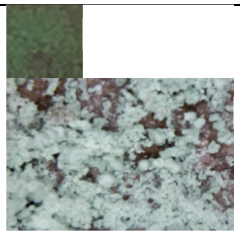
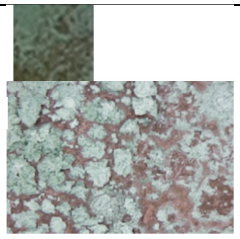
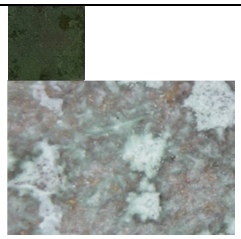
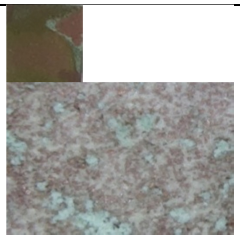
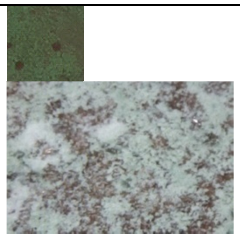
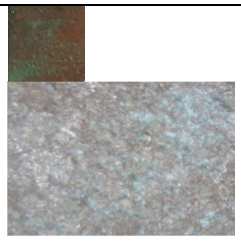
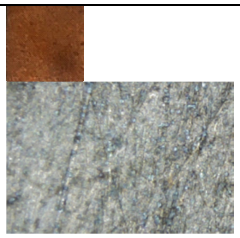
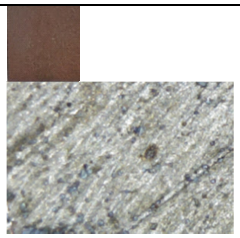
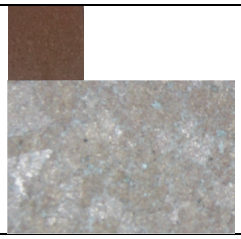
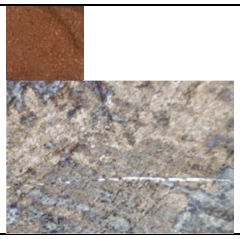
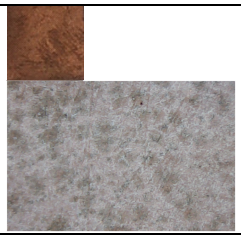
Tannin concentration plays important role in copper corrosion inhibition in 1 M HCl solution. Corrosion rate tend to decrease with the addition of tannin concentration but increase by the increase of temperature. The effect of tannin concentration extracted from raw gambier on the activation energy of copper corrosion was increased whereas activation energy of blank inhibitor was the lowest (Table 1).

Table 1. Activation Energy Value with Different Tannin Consentration in 24 Hours at 303 K, 313 K, 318 K and 323 K

Inhibitor Concentration (%)	Activation Energy (J/mol)	R^2
0.00	6,285	0.864
0.50	26,347	0.914
0.75	31,551	0.858
1.00	28,749	0.892

Low activation energy will make corrosion process run easily as the energy needed by the system to react only in small value. From all consentration, the best tannin consentration was 0.75%. The conformation of the result can be seen on the appearance of the copper plate which has not change into bluish green color especially in 0.75% and 1.00% inhibitor concentration (Table 2). In blank sample, all of samples changed into bluish green which detected as corrosion material. Some of compounds which is commonly formed by the reaction between copper and chloric are atacamite, paratacamite, botallacite and natokite (Sherif, 2012).

Table 2. The Effect of 1 M HCl on Copper Surface Appearance in 24 Hours

Inhibitor Concentration	Repetation		
	1	2	3
0.00%	 * **		
0.50%			
0.75%			
1.00%			

* 1x zoom
* 400x zoom

3. Conclusions

Tannin extracted from raw gambier, areca nut and mangosteen peel have ability to inhibit corrosion in copper. Inhibitor based raw gambier tannin was the best inhibitor for copper in HCL 1 M compared to the areca nut and mangosteen peel tannin. An addition of 0.75% inhibitor was found as the most effective inhibitor against HCL solution that resulted in the highest activation energy and good surface appearance on copper plate.

References

Anggraini T., Tail A., Yoshino T. and Itani T. Antioxidative activity and catechin content of four kinds of Uncaria gambir extracts from West Sumatra. Indonesia African Journal of Biochemistry Research Vol. 5(1), pp. 33-38, January 2011

Copper Development Association. (2014). Annual Data Copper Suply and Consumption [online]. Available: www.copper.org/resources/market_data/pdfs/annual_data.pdf (2 January 2015)

Fouda A.S., Wanees S., Modrek A. (2011). Some benzimidazolederivatives as corrosion inhibitors for copper in nitric acid. *International Journal of Corrosion*. Hindawi Publishing Corporation

Ibrahim M.N.M., Nadiyah M.Y.N., Amirul AA. (2005). Extraction of tannin in oil palm empty fruit bunch as

rust deactivator. *Material Science and Engineering* (2005) 197-201.
Kairi N.I. and Kassim J. (2013). The Effect of temperature on the corrosion inhibition of mild steel in 1 m HCl solution by *Curcuma longa* extract. *International Journal of Electrochemical Science*. 8 (2013) 7138 - 7155
Loto C.A. (2011). Inhibition effect of tea (*Camellia sinensis*) extract on the corrosion of mild steel in dilute sulphuric acid. *Journal of Material Environmental Science*. 2 (4) (2011) 335-344 ISSN : 2028-2508.
Obot I.B., Obi-Egbedi N.O., Umoren S.A. (2009). Adsorption characteristics and corrosion inhibitive properties of clotrimazole for aluminium corrosion in hydrochloric acid. *International Journal of Electrochemical Science*. 4 (2009) 863 – 877
Peres R.S., Cassel E., Azambuja D.S. (2012). Black wattle tannin as steel corrosion inhibitor. International Scholarly Research Network. *ISRN Corrosion*. Volume 2012, Article ID 937920, 9 pages doi:10.5402/2012/937920
Shah A.M., Rahim A.A., Yahya S., Raja P.B. (2011). Acid corrosion inhibition of copper by mangrove tannin. *Pigment& Resin Technology 40/2* (2011) 118–122
Schmitt G. (2009) . Global needs for knowledge dissemination, research, and development in materials deterioration and corrosion control. World Corrosion Organization Worldwide rights reserved
Sherif E.M. (2012) .Electrochemical and gravimetric study on the corrosion and corrosion inhibition of pure copper in sodium chloride solutions by two azole derivatives. *International Journal of Electrochemical Science*. (2012)1482 - 1495
Suttirak W. and Manurakchinakorn S. (2014). In vitro antioxidant properties of mangosteen peel extract. J Food Sci Technol. 2014 Dec;51(12):3546-58. doi: 10.1007/s13197-012-0887-5. Epub 2012 Nov 23.
Xing Z., Jiau W., Zhuang H., Wen-li M* and Hao-fu D. (2010). Antioxidant and Cytotoxic Phenolic Compounds of Areca Nut(Areca catechu). Chem. Res. Chinese Universities 2010, 26(1), 161—164
Zarrouk A., Hammouti B., Zarrok H., Al-Deyab S.S., Messali M. (2011). Temperature effect, activation energies and thermodynamic adsorption studies of l-cysteine methyl ester hydrochloride as copper corrosion inhibitor in nitric acid 2m. International Journal of Electrochemical Science. 6 (2011) 6261 – 6274

The IISTE is a pioneer in the Open-Access hosting service and academic event management. The aim of the firm is Accelerating Global Knowledge Sharing.

More information about the firm can be found on the homepage:
http://www.iiste.org

CALL FOR JOURNAL PAPERS

There are more than 30 peer-reviewed academic journals hosted under the hosting platform.

Prospective authors of journals can find the submission instruction on the following page: http://www.iiste.org/journals/ All the journals articles are available online to the readers all over the world without financial, legal, or technical barriers other than those inseparable from gaining access to the internet itself. Paper version of the journals is also available upon request of readers and authors.

MORE RESOURCES

Book publication information: http://www.iiste.org/book/

Academic conference: http://www.iiste.org/conference/upcoming-conferences-call-for-paper/

IISTE Knowledge Sharing Partners

EBSCO, Index Copernicus, Ulrich's Periodicals Directory, JournalTOCS, PKP Open Archives Harvester, Bielefeld Academic Search Engine, Elektronische Zeitschriftenbibliothek EZB, Open J-Gate, OCLC WorldCat, Universe Digtial Library , NewJour, Google Scholar