



Effectiveness of varieties in organic plant extracts of Durian as inhibitors on copper corrosion

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KEYWORDS	ABSTRACT
Corrosion resistance Corrosion inhibitor Plant extraction C-dot Durian	Facile synthesis of carbon dots from varieties of durian can be implemented with its application as an environmentally friendly inhibitor against copper corrosion. Durian can be processed as an organic plant inhibitor, but there is still no strong agreement whether the same variety has the same effectiveness. Therefore, C-dots were synthesized on Bintana and Monthong Durian extracts on copper. The synthesized C-dots were measured by weight loss and adsorption isotherm measurement and characterized by infrared (IR), UV-visible, and fluorescence spectroscopy. The corrosion rates of Bintana and Monthong Durian extract have a minimum value of $3.07 \times 10^{-3} \text{ mg cm}^{-2} \text{ h}^{-1}$ and $1.74 \times 10^{-3} \text{ mg cm}^{-2} \text{ h}^{-1}$ at 1000 ppm as optimum concentration. The inhibition efficiencies of Bintana and Monthong Durian extract have a maximum value of 62% and 78% at 1000 ppm as optimum concentration. Investigation of adsorbed layers on Cu surfaces also proves that adsorption of corrosion inhibitors satisfies the Langmuir and Freundlich adsorption isotherm, identifying the existence of monolayer adsorption on homogeneous sites and multilayer adsorption on heterogeneous sites. Hydrophilic groups are abundant on the surface of C-points such as C=O, O-H, and S=O, thus reflecting their potential as corrosion inhibitors.

Received 29 February 2024; received in revised form 21 July 2024; accepted 25 August 2024.

To cite this article: Lubis et al (2024). Effectiveness of varieties in organic plant extracts of Durian as inhibitors on copper corrosion. Jurnal Tribologi 42, pp.231-248.

1.0 INTRODUCTION

Metal corrosion is a problem that occurs in every country and generally costs developed or industrialized countries a percentage of their gross domestic product. Metal corrosion has led to large annual losses in the United States (Koch et al., 2002). Therefore, the development of satisfactory protective coatings continues to be of paramount importance to reduce losses from the effects of metal corrosion (Beving et al., 2007). Preventing steel corrosion during construction usually costs less than repairing steel bars that corrode during use (Wang et al., 2020). Corrosion is perhaps the most common undesirable phenomenon that causes metals to become weaker (Zhu et al., 2020; Mai et al., 2016). The factor is caused by contact of the metal surface with dissolved carbon dioxide, hydrogen sulfide, and salt (Bardal, 2004).

Corrosion inhibitors are liquid compounds that are compressed by a certain mechanism into the working fluid and absorbed into a surface chemically or mechanically or a combination of both to prevent the continuous dissolution of the material (Zunita et al., 2012; Hossain et al., 2022; Akintola et al., 2019; Ayoola et al., 2022; Cao, 1996). Inhibition of corrosion in metals has become a major challenge in most heavy industries. The main focus is on slowing down the extensive corrosion of various parts of oil production plants, pipes, and tubing of wellhead equipment (Al-Otaibi & Hammud, 2021). Adsorption inhibitors as corrosion inhibitors have been applied in various devices and technologies such as the petrochemical industry, chemical storage containers, preservation methods for acid and scale, as well as petrochemicals (Guo et al., 2017; Zaferani et al., 2013).

Corrosion inhibitors are divided into organic and inorganic corrosion inhibitors (Muñoz et al., 2004). Nitrite, molybdate, zinc salt, chromate, tungstate and other oxidizing inorganic substances are some examples of inorganic corrosion inhibitors (Li et al., 2022). Organic corrosion inhibitors include mainly organic compounds with heteroatoms (oxygen, nitrogen, sulfur, and phosphorus), as well as π bonds (Raja et al., 2016). However, their function as a corrosion inhibitor is less applicable due to the effect of environmental pollution based on Hinton's 1995 study (as cited in Gschneidner & Eyring, 1995) and El-Tabesh et al. (2020). The world is becoming more aware of environmental issues and the toxic impact of chemicals used in various industries. Currently there is increasing attention to environmentally friendly corrosion inhibition and the term green corrosion inhibitor has been coined due to the unique properties, such as renewable, efficient and biodegradable (Umoren & Eduok, 2016; Hu et al., 2016; Dakhil et al., 2018; Raghavendra, 2019; Ji et al., 2015). These environmentally friendly inhibitors can be acquired from various parts of different plants in extract solution (Al-Otaibi & Hammud, 2021) including bark, leaves, fruit, bark, seeds, roots, flowers and even whole plant extracts (Schreiner & Huyskens-Keil, 2006; Khanari et al., 2017). Previous studies have investigated the corrosion inhibitors made by plant extracts, such as banana (Guo et al., 2021), mangrove (Lubis & Dahlan, 2020) and pumpkin (Radi et al., 2021).

Carbon dot (C-dot) is a new member of carbon-based nanomaterials that emits fluorescence and was obtained during the purification of single-walled carbon nanotubes in 2004 (Xu et al., 2004), with a particle size of lower than 10 nm (De & Karak, 2013). C-dots have gradually become an important nanomaterial due to their extraordinary fluorescent properties, excellent water solubility, biocompatibility, biodegradability, low cytotoxicity, easy functionalization, and environmental friendliness, so they have been widely applied in optoelectronic devices, sensors, among others. biological model, and biomedical labeling (Sharma et al., 2017). C-dots can be easily produced by a simple method with cheap, renewable and abundant carbon precursors (De & Karak, 2013).

Durian is perfect as a source of C-dot because it contains sugars such as maltose, sucrose, glucose, and fructose as carbon sources; along with short-chain alkanethiols and hydrogen sulfide as volatile components which act as self-passivation for C-dots (Aziz & Jalil, 2019; Li et al., 2016). However, of various species of Durian, only the *Durio zibethinus* species is widely planted and harvested (Brown, 1997). In fact, several varieties of this species have been registered as recommendations for commercial planting in several countries, each with its own uniqueness (Aziz & Jalil, 2019). Previous study by Anindita et al. (2018) has succeeded in illustrating Durian's potential from its C-dot as an anti-corrosion material with 85.84% as a maximum value of inhibition efficiency at 800 ppm as inhibitor concentration. However, the study still did not identify which type of Durian was studied so the actual result is still debated. Apart from that, C-dot has been synthesized from durian juice with random type as a carbon precursor. This compound is a suitable precursor as a surface passivation agent of C dot. The excess of sulfur-based groups on the C-dot surface can produce strong adsorption interactions with the metal in the corrosion inhibitor properties (Larabi et al., 2006). Furthermore, the carbonyl groups on the C-dot surface originate from carbohydrate precursors which have a dipole character and show significant intermolecular interactions between molecules adsorbed on a surface of any metals so that the corrosion inhibitor properties are increased (Mihajlović et al., 2017).

Individual plants with different species are chemically rich with diverse chemical compositions in the same genus (Swanson, 1995). The same speciality also happens between durians (Brown, 1997). Therefore, a study to investigate the corrosion inhibitor properties of different extract plants by various species in the same genus is essential. The study uses two similar durian species, Bintana and Monthong Durian, which are officially registered in different countries to highlight their uniqueness as a corrosion protection agent. These two durian varieties are included in *Durio zibethinus* Murr. or *Durio zibethinus* Linnaeus (Amid et al., 2012), each of which has unique characteristics with 455/Kpts/SR.120/4/2008 as an identity on a certificate number by Direktorat Jenderal Hortikultura Kementerian Pertanian Republik Indonesia (2023) for Bintana Durian and D159 as the variety code by the Department of Agriculture, the Government of Malaysia for Monthong Durian based on Husin et al. (2018).

In this study, the C-dot inhibition efficiency of Bintana and Monthong Durian were tested against copper corrosion in a solution of 1% NaCl using various concentrations of inhibitors. The corrosion inhibition efficiency is detected by weight loss measurement. In addition, the calculation for the adsorption isotherms is used to manifest interaction degree between molecules of the inhibitors on the metal surface, along with performing Fourier-Transform Infrared Spectroscopy to identify and characterize the unknown materials. The study also investigated absorbance spectrum and carbon dot emission by Ultraviolet/Visible (UV/Vis) spectrophotometer and photoluminescence spectroscopy, respectively.

2.0 EXPERIMENTAL PROCEDURE

The experimental procedures for this study are divided into several stages. An overview of the procedure can be seen in Figure 1, while a detailed explanation of the procedure can be seen in each sub-chapter. Separately, almost the entire procedure is explained in detail in sub-chapters which are divided into materials preparation for making C-dot, preparation of NaCl corrosive medium, making a corrosive medium solution by adding C-dot durian, preparation for weight loss and adsorption isotherm measurement, measurement of Fourier-Transform Infrared spectroscopy, fluorescence and absorbance analysis

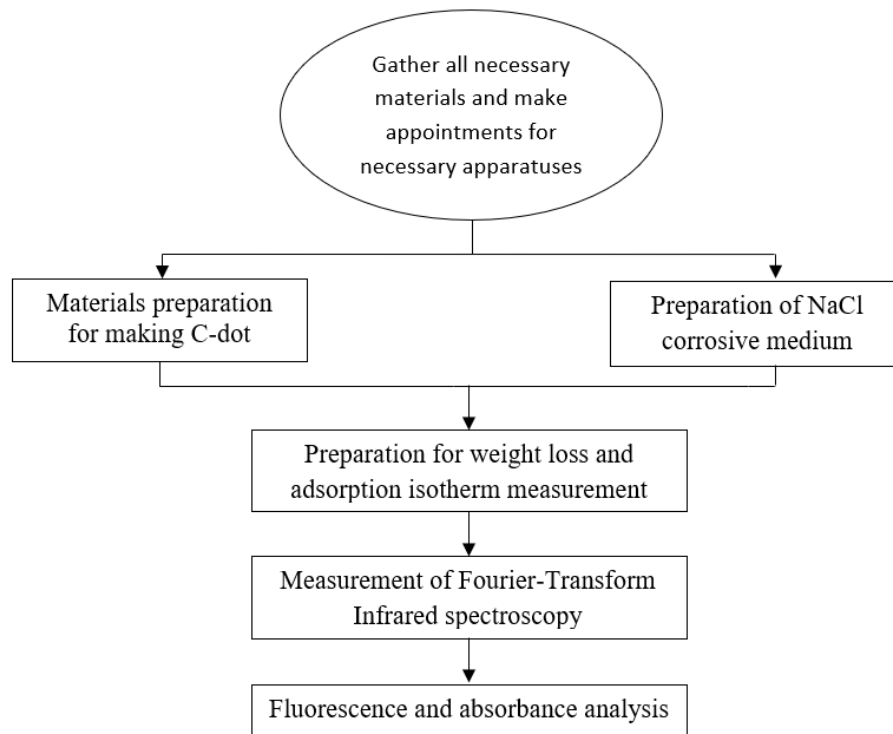


Figure 1: Flowchart for experimental procedure

2.1 Materials Preparation for Making C-Dot

The main materials were Bintana and Monthong Durian fruit from Ciroyom, Bandung, West Java Province, Indonesia; copper plate made by PT. Metal Elindo; sodium chloride by Merck; a solution of 96% ethanol; distilled water; acetone and sandpaper. The durians picked from trees are between 4 to 5 months old.

C-dot is synthesized by simple heating of durian juice. A number of 80 grams of durian flesh was separated from the seeds and then made into a paste using 100 mL of distilled water. Then 120 mL of grain-free juice was taken and then added with 120 mL of ethanol. After that, this solvent was put in a Durian bottle and heat using an oven at a constant temperature of 125°C for 12 hours. After that, the dark brown product was cooled to room temperature and dissolved in 120 mL of distilled water. The separation of residue was done by filtration, then 200 mL of ethanol was mixed into the filtrate. The filtrate was centrifuged for 15 minutes so that there is a separation of large particles. After that, the solvent was evaporated at a temperature of 80°C to obtain C-dots. The same procedure was conducted for both durian fruits.

2.2 Preparation of NaCl Corrosive Medium

Sodium chloride stock solution with 5% concentration is made by weighing 5 grams of NaCl crystals and then dissolving them using distilled water in a 100 mL flask. Then 10 mL stock solution of NaCl with 5% concentration was pipetted into a 50 mL beaker and then diluted to obtain 1% NaCl by adding distilled water and durian extract solution.

2.3 Making a Corrosive Medium Solution by Adding C-Dot Durian

C-dot was weighed as much as 0.2 g and then dissolved in 100 mL of distilled water to obtain a concentration of durian extract mother liquor of 2000 ppm. The mother liquor of durian extract was then poured into a beaker of 50 mL for concentrations of 200 ppm, 400 ppm, 600 ppm, 800 ppm and 1000 ppm with volumes of 5 mL, 10 mL, 15 mL, 20 mL and 25 mL respectively. The solution of varying concentrations was then mixed with 10 mL of 5% NaCl stock solution. Next, 50 mL of distilled water is poured into the mixture using a beaker.

2.4 Preparation for Weight Loss and Adsorption Isotherm Measurement

The weight loss measurement is a general and simplest method to detect corrosion inhibition efficiency. Many properties of solids are changed by corrosion, such as mass, magnetic flux, electrical resistance, and mechanical properties. Corrosion monitoring and investigation of environmental conditions that cannot be simulated in the laboratory are very effectively conducted using the weight loss measurement which is also useful to calculate corrosion inhibition efficiency. In the low-cost method, a small sample is dipped in certain corrosive media for certain period and then removed from the environment. The difference in mass before and after immersion is important. The estimation of corrosion rate in this method is determined by Equation (1).

$$v_{corr} = \frac{K (W_1 - W_2)}{A (t_1 - t_2) \rho} \quad (1)$$

where v_{corr} symbolizes the quantity for the corrosion rate, K is corrosion rate constant which is proportional to 8.76×10^4 mm/year, A is total surface area (cm^2), W_1 and W_2 are the initial and final mass (g), ρ is density of the test object (8.96 g/cm^3), t_1 and t_2 are the start time and end time (h), respectively.

Copper plate specimens were prepared with 2x2 cm as their sizes and 1 mm as their thicknesses. The copper is cleaned and the surface is smoothed with sandpaper and then rinsed with distilled water. Then rinse with acetone to remove the fat attached to the copper. Next the steel is dried. After drying, the steel is weighed and the weighing results are expressed as initial mass (w_1). The weighed copper was then soaked in 50 mL of 1% NaCl corrosive medium solution with various concentrations of durian extract for 14 days (336 hours) at room temperature. After that, the copper was cleaned and washed with distilled water and acetone. Then it is dried and then weighed and the weighing results are expressed as final mass (w_2). The stages were repeated five times at each concentration.

After the rate of a corrosion process is calculated, the step was continued with the ascertainment of the value for inhibition efficiency. In this method, the inhibition efficiency is determined by Equation (2).

$$\eta_w = \frac{v_{corr}^0 - v_{corr}}{v_{corr}^0} \times 100\% \quad (2)$$

where η_w symbolizes the quantity for inhibition efficiency, v_{corr}^0 and v_{corr} are corrosion rates without and with inhibitors at certain concentration levels, respectively.

The measurement for corrosion rate calculation as well as inhibition efficiency calculation on copper is conducted by two steps with and without the coating extracts as inhibitors in a solution

of NaCl at 1% concentration set at room temperature. Measurements and calculations with these inhibitors were carried out with concentrations of 200 ppm, 400 ppm, 600 ppm, 800 ppm, and 1000 ppm.

Corrosion resistance measurements also take further the adsorption isotherm into consideration. In this case, the Langmuir and Freundlich adsorption isotherms will be applied as two adsorption isotherms in this study. Surface coverage (θ) is then a parameter for the adsorption isotherms. This surface coverage will be maximum (saturation) of a particular adsorbate on a particular surface whose value is always one, $\theta_{max} = 1$. Therefore, calculation for surface coverage values can be done using equation (3).

$$\theta = \frac{v_{corr}^0 - v_{corr}}{v_{corr}^0} \tag{3}$$

Where v_{corr}^0 and v_{corr} have the same definition as when calculating inhibition efficiency.

The metal surface filled with the adsorbed layer on the Langmuir isotherm has a size of one molecular diameter as its thickness and the adsorption process is possible to occur at a certain number of local sites (Foo & Hameed, 2010). These sites for localized equilibrium adsorption are similar to each other and there are no interactions or vacancies between molecules regularly adsorbed on these sites. Therefore, the adsorption of Langmuir isotherm applies validly for homogeneous adsorption processes. The similar adsorption enthalpy together with the free energy is possessed by the adsorbate because of the same adsorption tendency at all sites (Kundu & Gupta, 2006). In addition, each site only accommodates one adsorbate because it has reached an equilibrium state and adsorption will not continue at this preoccupied site. In each case, surface coverage values taken from experimental data will be compared with the proposed adsorption isotherm model. The Langmuir isotherm, which fits the experimental data, can be given as Equation (4).

$$K_{ads} C = \frac{\theta}{1 - \theta} \tag{4}$$

where θ is the coverage of fractional surface by molecules of corrosion inhibitor, K_{ads} is the equilibrium constant of the adsorption process and C is the concentration of the corrosion inhibitor. Equation (4) can be rearranged into the following equation to show the relationship between the coverage of surface and the concentration of corrosion inhibitor schematically.

$$\frac{C}{\theta} = C + \frac{1}{K} \tag{5}$$

The surface coverage values were plotted as a function of the concentration for corrosion inhibitor and then the different adsorption isotherms were compared with the data from experiments to find the most suitable adsorption isotherm. The Freundlich isotherm describes a nonideal and reversible adsorption process in which the adsorbed layer thickness can exceed a single layer thickness. The interpretation of multilayer adsorption processes can use that experimental model. In this concern, heterogeneity arise in their adsorption energies and the active sites distribution (Adamson & Gast, 1967; Fateh et al., 2017). It can be said that the adsorption energy is equal to the total adsorption energy of the adsorption site with the binding energy. Initially, adsorption sites with stronger bonds will be occupied which in turn causes an exponential decrease in the adsorption energy as the adsorption process is completed (Fateh et

al., 2017). The Freundlich adsorption isotherm is widely used, especially for organic compounds in heterogeneous systems.

The degree of surface coverage by corrosion inhibitor species and the concentration of corrosion inhibitors in the Freundlich adsorption isotherm are determined by equation (6).

$$\theta = k C^{(1/n)} \quad (6)$$

If the logarithmic value for surface coverage is plotted as a function of the logarithmic value of the value for corrosion inhibitor, the variation of $\log C / \theta$ versus $\log C$ with the slope of n denotes that the adsorption of the corrosion inhibitor adheres to the Freundlich isotherm. Figure 9 describes the surface coverage variation respecting the concentration solution for durian fruit extract as an example of the Freundlich adsorption isotherm in corrosion inhibitor (Krishnaveni & Ravichandran, 2015).

2.5 Measurement of Fourier-Transform Infrared Spectroscopy

The characterization of steel surface was determined by Fourier-Transform Infrared Spectroscopy (Universal ATR-FTIR, PerkinElmer Frontier C90704 Spectrum IR Version 10.6.1), which extended from 600 cm^{-1} to 4000 cm^{-1} with sweep spacing of 500 cm^{-1} , using KBr disk technique. The samples of FTIR characterization were mixed uniformly with KBr and made into the disk. Light source, beam splitter and detector that were used in FTIR spectroscopy are ceramics, potassium bromide (KBr) and deuterated L-alanine doped triglycene sulphate (DLATGS), respectively.

2.6 Fluorescence and Absorbance Analysis

The fluorescence measurements are carried out using a Hitachi F-2700 fluorescence spectrophotometer. Meanwhile, the absorbance measurements are carried out using a N4S UV-VIS spectrophotometer. The extraction concentrations of Bintana and Monthong Durian are the same as each other at 0.25 ppm for 1% NaCl solution. The spectra resulting from the fluorescence emission of these solutions were recorded between 400 and 700 nm with an excitation wavelength of 366 nm. For absorbance spectra of these solutions, it was recorded between 200 and 800 nm.

3.0 RESULTS AND DISCUSSION

The results and discussion in this study include processing of durian fruit for c-dot synthesis, effect of durian extract concentration, study of the Langmuir and Freundlich adsorption isotherms, infrared spectra of carbon dots, absorbance spectra, and fluorescence emission measurements. The analysis that has been carried out is based on the results of both calculations and measurements by the apparatus.

3.1 Processing of Durian Fruit For C-Dot Synthesis

Bintana and Monthong Durian have green skin and sharp spines. The flesh of Bintana durian is pale yellow and the seeds are large and hard, while the flesh of Monthong Durian is bright yellow, tastes sweet and the seeds are small as in Figure 2.

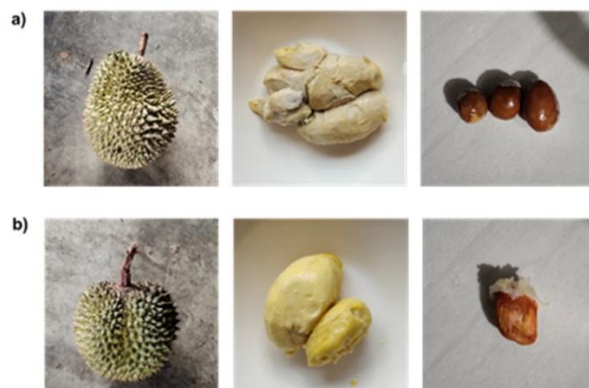


Figure 2: Durian fruit a) Bintana, b) Monthong.

C-dot is synthesized by heating durian juice which contains carbohydrates such as glucose, maltose, sucrose and fructose as a source of carbon. Heating the durian solution produces a product that is dark brown in color. The resulting product is soluble in water. The synthesis scheme is in Figure 3.

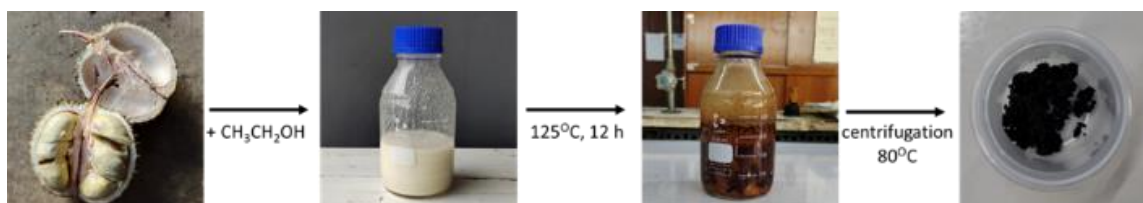


Figure 3: Scheme of c-dot synthesis Monthong Durian.

The C-dot in durian inhibits the rate of corrosion on copper. Furthermore, copper must be in a certain corrosive medium.

3.2 Effect of Durian Extract Concentration

C-dot from Bintana and Monthong Durian inhibits the corrosion rate of copper in the corrosive medium of 1% NaCl. The corrosion rate value is lower with the coating of durian extract at certain concentration. Monthong Durian extract has the ability to inhibit corrosion rates greater than Bintana Durian extract. The effect of durian extract concentration on corrosion rate is displayed in Figure 4. The corrosion rate of copper in NaCl medium without the presence of durian extract has a value of $8.06 \times 10^{-3} \text{ mgcm}^{-2}\text{h}^{-1}$. However, the final corrosion rate at 1000 ppm as optimum concentration has a value of $3.07 \times 10^{-3} \text{ mgcm}^{-2}\text{h}^{-1}$ with Bintana Durian extraction and $1.74 \times 10^{-3} \text{ mgcm}^{-2}\text{h}^{-1}$ with Monthong Durian extraction.

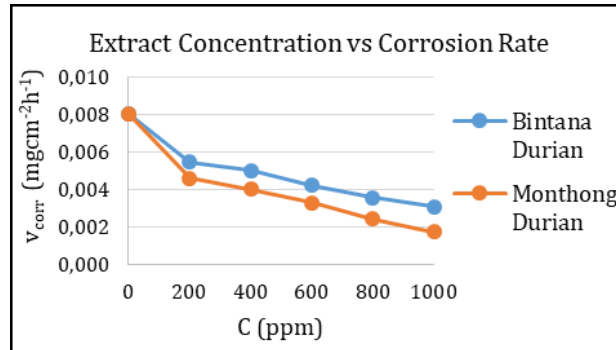


Figure 4: Graph of the effect of durian extract concentration on corrosion rate.

The inhibition efficiency value of durian extract was higher with increasing extract concentration. The extract inhibition efficiency of Monthong Durian has a higher value than Bintana Durian. The next level of corrosion protection effectiveness is the inhibition efficiency value which depends on the corrosion rate parameter which can be seen in Figure 5.

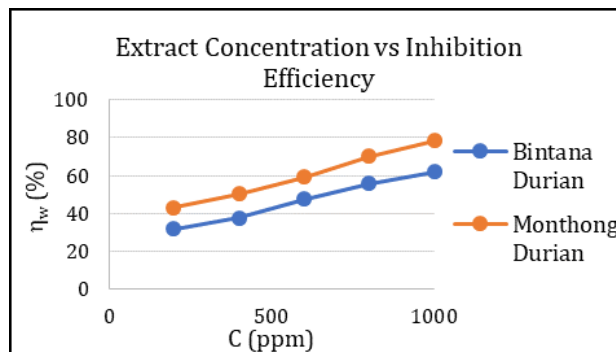


Figure 5: Graph of the effect of durian extract concentration on inhibition efficiency.

The percentage value for inhibition efficiency of Bintana Durian extract at 200 ppm was 32% and at 1000 ppm was 62%. Monthong Durian extract has an inhibition efficiency at concentrations of 200 ppm and 1000 ppm, namely 43% and 78%. These indicate that Monthong Durian has better inhibition efficiency compared to Bintana Durian. Nevertheless, these results are still lower than the previous study with durian that was not identified by Anindita et al. (2018), which was 86% using 800 ppm C-dot.

Then the effect of extract concentration on weight loss can be observed in Figure 6. The weight loss of Bintana Durian is greater at the same extract concentration compared to Monthong Durian. Weight Loss in the sample indicates that there is surface erosion of the copper by corrosive substances which results in the loss of some of the density of a copper sample. The partial loss of density also affects the weight loss of copper. With the results of a smaller corrosion rate, greater inhibition efficiency, and greater weight loss, all these data indicate that Monthong Durian has better effectiveness in all parameters as a corrosion inhibitor in corrosion protection on copper

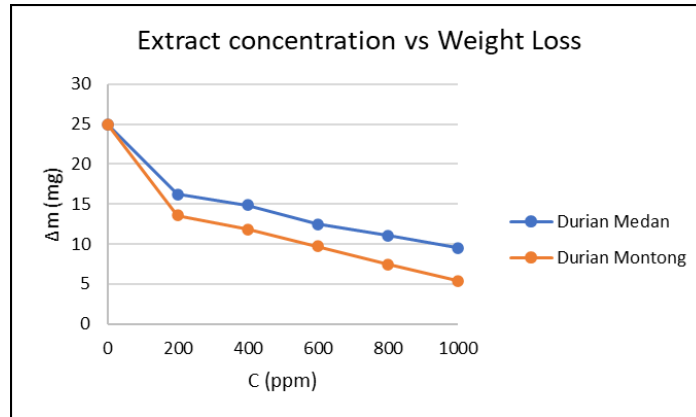


Figure 6: Graph of the effect of durian extract concentration on weight loss.

3.3 Study of the Langmuir and Freundlich adsorption isotherms

Figures 7 and 8 describe the Langmuir and Freundlich adsorption isotherms for the Bintana and Monthong Durian corrosion inhibitors on copper surfaces. Both Langmuir and Freundlich adsorption isotherms rely on surface coverage values that are rooted in weight loss measurements (Scendo, 2008). A good and understandable correlation was obtained based on Figure 7 and 8 with the line slope approaching one. The line slope determines the equilibrium constant of the adsorption process or the K_{ads} parameter value. The experimental data which have good proportionality with the Langmuir adsorption isotherm shows the fact that the adsorption of corrosion inhibitors adhere to the Langmuir isotherm, indicating strong agreement for the existence of monolayer adsorption on homogeneous sites. Meanwhile, the adsorption of corrosion inhibitors attached to the Langmuir isotherm is shown by experimental data to have good proportionality with the Langmuir adsorption isotherm, so this indicates strong agreement with the existence of multilayer adsorption on heterogeneous sites.

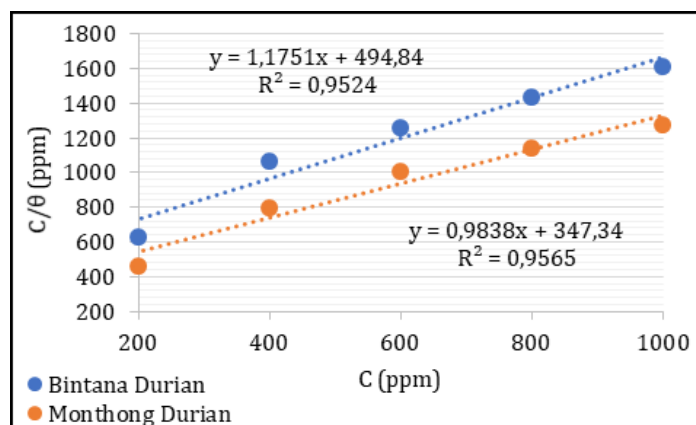


Figure 7: Graph of Langmuir adsorption isotherm.

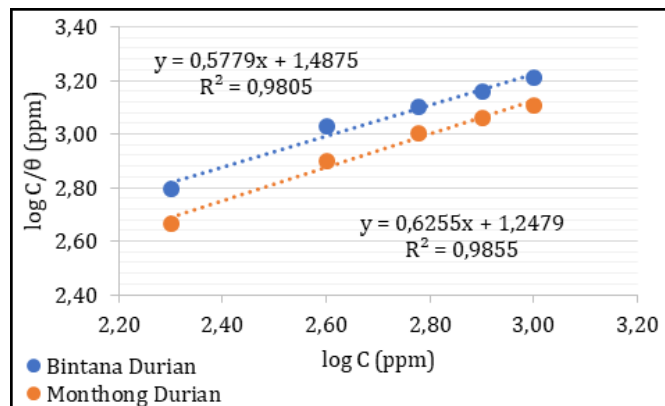


Figure 8: Graph of Freundlich adsorption isotherm.

If the general outline is drawn as a conclusion, the adsorption isotherm calculation produces a correlation coefficient (R^2) on the Langmuir isotherm of 0.9524 for Bintana Durian and 0.9565 for Monthong Durian, as well as on the Freundlich isotherm of 0.9805 for Bintana Durian and 0.9855 for Monthong Durian. Then the K_{ads} value based on the Freundlich adsorption isotherm is 30.7256 ppm for Bintana Durian and 17.6970 ppm for Monthong Durian. In essence, the adsorption compliance of Monthong Durian extract with the Freundlich and Langmuir adsorption isotherms is better than the adsorption of Bintana Durian extract, However, both of them identified strong evidence of homogeneous and heterogeneous sites on durian. Meanwhile, homogeneous and heterogeneous sites on durian that show monolayer and multilayer adsorption will later be identified in the infrared spectra of carbon dots by FTIR.

3.4 Infrared spectra of carbon dots

The infrared spectra of carbon dots are analyzed using FTIR as in Figures 9 and 10 for Bintana and Monthong Durian, respectively. The spectra will then identify structural information about the C-dot surface functionalization in the form of abundant hydrophilic groups, carbonyl groups as well as the Heterocyclic compounds.

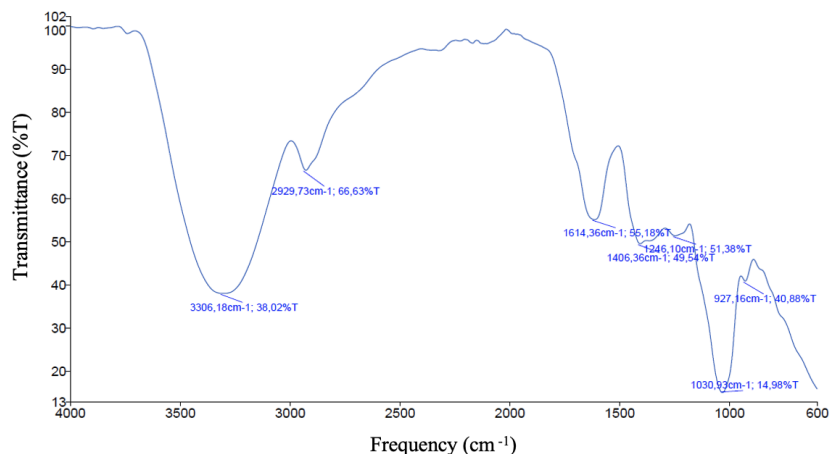


Figure 9: Graph of infrared spectrum for Bintana Durian.

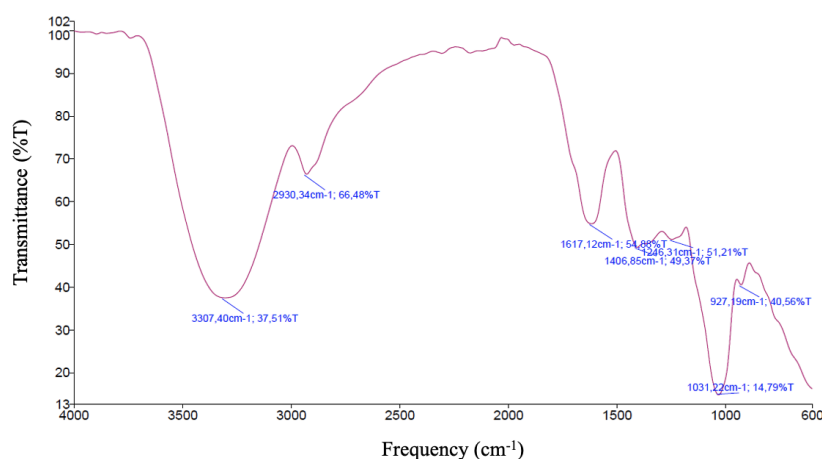


Figure 10: Graph of infrared spectrum for Monthong Durian.

FTIR analysis is carried out for obtaining structural information about the C-dot surface functionalization. Abundant hydrophilic groups for Bintana Durian are shown by the spectrum stretching frequencies at 3306.18, 2929.73, 1614.36, 1406.36, 1246.10, 1030.93, and 927.16 cm^{-1} respectively revealing the existence of $-OH$, $-C$ groups. $-OH$, $C-H$, $C=O$, $C=C$, $C-O-C$, $S=O$, and epoxy rings. Meanwhile, Abundant hydrophilic groups for Monthong Durian are shown by the spectrum stretching frequencies at 3307.40, 2930.34, 1617.12, 1406.85, 1246.31, 1031.22, and 927.19 cm^{-1} respectively revealing the existence of $-OH$, $-C$ groups. $-OH$, $C-H$, $C=O$, $C=C$, $C-O-C$, $S=O$, and epoxy rings. In this case, Bintana Durian has a higher transmittance than Monthong Durian for each Abundant hydrophilic group. On the other hand, Monthong durian has a higher frequency than Bintana Durian for each Abundant hydrophilic group.

The functional groups in Durian base material are different based on the formation of carbonyl groups in the synthesized C-dot. The absence of carbonyl absorption in durian indicates that the carbonization reaction at the C-dot has been successful. The presence of this functional group supports that the synthesized C-dot has excellent solubility in water (De & Karak, 2013). Furthermore, C-dot surface functionalization, especially sulfur-based groups, is very useful for material interactions with copper surfaces.

Heterocyclic compounds with sulfur-based groups have been applied as organic inhibitors of copper corrosion. The compounds of 2-mercapto-1-methylimidazole showed good corrosion inhibitory activity for steel carbon in 0.5 M hydrochloric acid (Larabi et al., 2006), the mercapto group could be chemically adsorbed on the Cu surface via the S atom (Tremont et al., 2000). Other studies have proposed that the interaction of S atoms with metal surfaces results in the generation of insoluble protective complexes (Qin et al., 2011). Therefore, S-functionalized C-dot from durian has corrosion-inhibitory activity on copper surfaces.

3.5 Absorbance Spectra and Fluorescence Emission Measurement

The measurement result of the absorbance spectra and fluorescence emission spectra for C-dot solution on durian extracts is displayed in Figure 11 and 12. Identification with the methods of absorption and emission cultivates information on the existence of many nanometer particles affected by the change of sensitive optical properties for the sizes, shapes, agglomerations and particle concentrations (Tomaszewska et al., 2013).

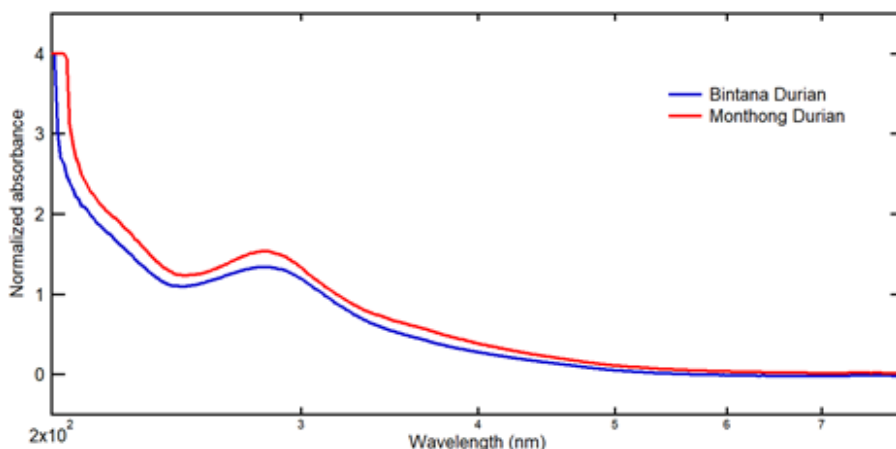


Figure 11: Graph of absorbance spectra.

The UV-Vis absorption spectra of the C-dot solution shows two strong absorption bands, the first peak at a wavelength of around 248 nm for Bintana and Monthong Durian indicates the π - π^* transition of the C=C bond. The band with a peak at around 282 nm for Bintana and Monthong Durian can be referred to the n- π^* transition indicating C=O bonding (De & Karak, 2013). The electronic transition that occurs at the C-dot shows the electrons excitation from the valence band to the conduction band. For the same wavelength range, Monthong Durian has a higher absorbance value than Bintana Durian.

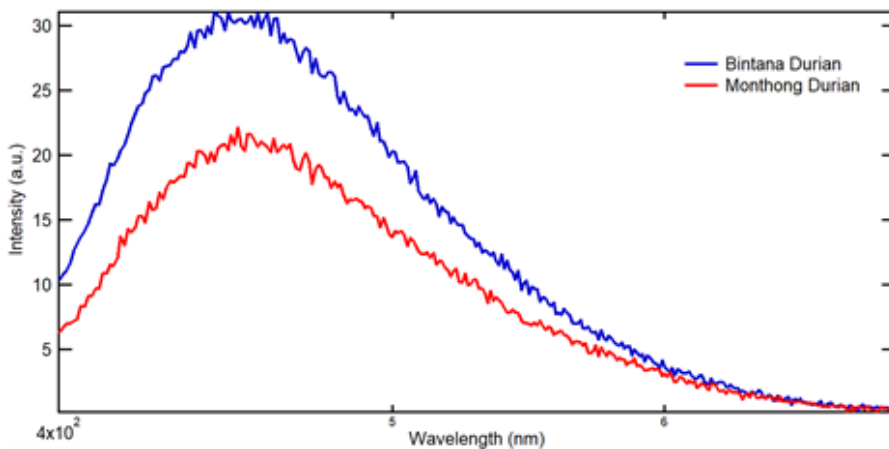


Figure 12: Graph of fluorescence emission spectra.

This transfer requires energy that corresponds to the width of the band gap of each compound. The wider the band gap of a compound, the greater the energy desired to stimulate an electron and the lower the wavelength absorbed by an electron (Lakowicz, 2006).

Electrons in π^* will relax to π due to electron instability at too high an energy level. The relaxation event is accompanied by the emission of light at a wavelength that is complementary to the wavelength absorbed during excitation. This event is often known as fluorescence. The

fluorescent emission spectra of the synthesized C-dot for Bintana and Monthong Durian shows maximum emission around 456 nm with a wide spectrum shape which has a higher intensity compared to C-dots made from citric acid without the accretion of a passivation agent. The origin of this strong emission may be due to the presence of several functional groups on the C-dot surface that act as emission traps for electronic transitions (De and Karak, 2013). Then for almost the entire same wavelength range as the origin of the strong emission, Monthong Durian has a higher fluorescence emission spectrum than Bintana Durian.

CONCLUSIONS

The efficiency of durian extract between Bintana and Monthong Durian was obtained through measuring weight loss and C-dot adsorption isotherm in 1% NaCl solution which is considered as an optimal choice for environmentally friendly inhibitors. Bintana Durian has a higher corrosion rate and lower inhibition efficiency than Monthong Durian. The corrosion rates of Bintana and Monthong Durian extract have a minimum value of $3.07 \times 10^{-3} \text{ mgcm}^{-2}\text{h}^{-1}$ and $1.74 \times 10^{-3} \text{ mgcm}^{-2}\text{h}^{-1}$, respectively, at 1000 ppm as optimum concentration. Meanwhile, the inhibition efficiencies of Bintana and Monthong Durian extract have a maximum value of 62% and 78%, respectively, at 1000 ppm as optimum concentration. These data imply that Monthong Durian is more effective as an organic inhibitor of plants on copper compared to Bintana Durian. However, the inhibition efficiency results are lower than previous study on unidentified durian with result of 86% using 800 ppm C-dot. Nevertheless, this study represents an important leap forward for further studies of plant varieties in certain applications, especially organic inhibitors in corrosion protection.

The adsorbed layer on the Cu surface with Bintana and Monthong Durian extraction also proves that the adsorption of corrosion inhibitors validates the Langmuir and Freundlich adsorption isotherms, where the adsorption compliance of Durian Monthong extract is better than the adsorption of Durian Bintana extract. In this case, the Langmuir adsorption isotherm indicates strong agreement that there is monolayer adsorption on homogeneous sites on durian, and the Langmuir adsorption isotherm indicates strong agreement that there is multilayer adsorption on heterogeneous sites on durian. For the homogeneous and heterogeneous sites on durian, these studies on infrared spectra of carbon dots reveal the existence of -OH, -C groups, -H, C=O, C=C, C-O-C, S=O, and epoxy rings. Based on its appearance with transmittance at a certain frequency, Bintana Durian has a higher transmittance than Monthong Durian for each abundant hydrophilic group. On the other hand, Monthong Durian has a higher frequency than Bintana Durian for each abundant hydrophilic group.

For absorption bands and electronic transitions, carbon dots can specifically be identified using the absorbance spectrum and the fluorescent emission spectrum. The $n-\pi^*$ transition indicating C=O bonding has appeared around 282 nm in the absorbance spectra of Bintana and Monthong Durian. The maximum emission is shown by the fluorescent emission spectra of the synthesized C-dot around 456 nm of Bintana and Monthong Durian. For the overall value, Monthong Durian has a higher absorbance value than Bintana Durian for the same wavelength range, meanwhile Monthong Durian has a higher fluorescence emission spectrum than Bintana Durian for almost the entire same wavelength range.

ACKNOWLEDGMENTS

This work is supported by the International Indonesian Scholars Association (I-4) with a Research Grant in November 2021.

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